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THz Technology and Molecular Interactions

### ABSTRACT

The purpose of this project was to explore opportunities from a fundamental physics point of view for the use of the THz spectral region for remote and point sensing. This work has included: (1) the development of compact solid state point sensors for chemical identification with ‘absolute’ specificity, (2) studies of the phenomenology that underlies imaging in the THz spectral region, (3) the demonstration of new system strategies for THz imaging based on this basic work, (4) A study of the use of Rydberg atoms as a photocathode for THz imaging (in analogy to ‘night vision’ schemes for the optical), (5) a study of the detectivity of gases in the head space above liquids in bottles, and (6) the development of a new approach to atmospheric remote sensing that transcends the fundamental problems associated with spectral broadening at atmospheric pressure.

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**List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

S. Albert and F. C. De Lucia, "Fast Scan Submillimeter Spectroscopy Technique (FASSST): A New Analytical Tool for the Gas Phase," *Chimia*, vol. 55, pp. 29-34, 2001

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D. T. Petkie, C. Casto, F. C. De Lucia, S. R. Murrill, B. Redman, R. L. Espinola, C. C. Franck, E. L. Jacobs, S. T. Griffin, C. E. Halford, J. Reynolds, S. O'Brien, D. Tofsted, "Active and passive imaging in the THz spectral region: phenomenology, dynamic range, modes, and illumination," *JOSA*, vol. B25, pp. 1523- 1531, 2008

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F. C. De Lucia, "The Submillimeter: A Spectroscopist's View," *J. Mol. Spec.*, vol. 261, pp. 1-17, 2010

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### **(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)**

F. C. De Lucia, "Science and Technology in the Submillimeter Spectral Region," *Optics and Photonics News* vol. 14, pp. 44-50, 2003

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F. C. De Lucia, "System Applications, Phenomenology, and Radiative Transfer," Submillimeter Wave Imaging Focal Plane Array Technology (DARPA) (Arlington, VA., 2003).

F. C. De Lucia, "The Science and Technology of the Submillimeter Spectral Region: Temperature, Energetics, and Probes," (Arizona State University, Tempe, AZ, 2000).

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F. C. De Lucia, "The Physics of the Submillimeter/THz: Applications, Opportunities, and Pitfalls," USAMDC (Huntsville, AL, 2004).

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F. C. De Lucia, "The Physics and Chemistry of Analysis in the Submillimeter/Terahertz Spectral Region," American Chemical Society (Washington, D.C., 2005).

F. C. De Lucia, "Millimeter, Nearmillimeter, Submillimeter, Terahertz, and Far Infrared Science and Technology and ARO: Past, the Present, but mostly the Future," Army Research Office (RTP, NC, 2005).

F. C. De Lucia, "Terahertz (Millimeter, Nearmillimeter, Submillimeter, Far Infrared) Science, Technology, and Opportunities," Lawrence Livermore National Laboratory (San Francisco, CA, 2005).

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F. C. De Lucia, "Signature Science in the Terahertz: The Second Gap in the Electromagnetic Spectrum," Optics East (Boston, MA, 2006).

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F. C. De Lucia, D. T. Petkie, R. K. Shelton, S. L. Westcott, and B. N. Strecker, "THz + 'X': a search for new approaches to significant problems," Terahertz for Military and Security Applications III (Orlando, FL, 2005).

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F. C. De Lucia, "Science and Technology with High Brightness CW Sources,"NSF-DOE Opportunities in THz Science Workshop (2004).	
E. Jacobs, R. G. Driggers, K. A. Krapels, F. C. De Lucia, and D. T. Petkie,"Terahertz Imaging Performance Model for Concealed Weapon Identification," Proc. SPIE 5619, pp. 98-107 (2004).	
F. C. De Lucia, and D. T. Petkie, "THz gas sensing with submillimeter techniques," Proc. SPIE 5790, 44-53 (2005).	
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D. T. Petkie, F. C. De Lucia, C. Corey, P. Helminger, E. L. Jacobs, S. K. Moyer, S. R. Murrill, C. E. Halford, S. T. Grif?n, and C. C. Franck, "Active and passive millimeter- and sub-millimeter-wave imaging," Proc. SPIE 5989, 18 (2005).	
F. C. De Lucia, D. T. Petkie, R. K. Shelton, S. L. Westcott, and B. N. Strecker, "THz + 'X': a search for new approaches to significant problems," in Terahertz for Military and Security Applications III Proc. SPIE 5790, 219 (2005).	
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F. C. De Lucia, "Spectroscopic Systems and Vacuum Electronics in the Submillimeter ," in Proceedings of 2010 IEEE Vacuum Electronics Conference (IVEC), 13-16 (2010).	
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Number of Manuscripts:	0.00

Patents Submitted	

Patents Awarded	

Awards	
2001 William F. Meggers Award of the Optical Society of America	

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### Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Rebecca Butler	
Andrey Meshkov	
Corey Casto	
Ivan Medvedev	
Joe Demers	
David Graff	0.00
<b>FTE Equivalent:</b>	<b>0.00</b>
<b>Total Number:</b>	<b>6</b>

---

### Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Markus Behnke	
Ivan Medvedev	
Ryan Bettens	
Sieghard Albert	
Markus Mengel	
Christopher Neese	0.00
<b>FTE Equivalent:</b>	<b>0.00</b>
<b>Total Number:</b>	<b>6</b>

---

### Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Frank C. De Lucia		No
Eric Herbst		No
Manfred Winnewisser		No
Brenda Winnewisser		No
<b>FTE Equivalent:</b>		
<b>Total Number:</b>	<b>4</b>	

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### Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
<b>FTE Equivalent:</b>	
<b>Total Number:</b>	

### Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: ..... 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

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The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ..... 0.00

### Names of Personnel receiving masters degrees

NAME

**Total Number:**

### Names of personnel receiving PhDs

NAME

Joe Demers  
Ivan Medvedev  
Rebecca Butler  
Andrey Meshkov

**Total Number:** 4

### Names of other research staff

NAME

PERCENT SUPPORTED

Douglas Petkie	No
Henry Everitt	No
Zibniew Kisiel	No
Cindy Carey	No

**FTE Equivalent:**

**Total Number:** 4

### Sub Contractors (DD882)



**Inventions (DD882)**

# **Terahertz Technology and Molecular Interactions**

**Frank C. De Lucia  
Department of Physics  
Ohio State University**

**December 15, 2010**

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## **I. Introduction**

This final report covers a number of interrelated research topics in what is variously called the millimeter, sub-millimeter, terahertz, or far infrared spectral region. In keeping with the title of this project, we will largely refer to this as the terahertz (THz) spectral region. These topics are connected by the high resolution, electronic technology that we originally developed for molecular spectroscopy, but which has evolved to support a variety of scientific and technical applications. The latter especially has been greatly aided by the development of a robust commercially available source and detector technology, which substantially increases the impact that the THz spectral region can have on the larger community. While there is considerable technical synergy and overlap among them, we will organize this report by the general topics: (1) Point sensors, (2) Remote sensors, (3) Imagers, (4) Multimode spectroscopy, and (5) Rydberg photocathodes.

This work has been of considerable interest within the DoD community and has led to a number of interactions and follow-on programs, and we will also discuss them. Finally, because there are a number of ongoing or nascent opportunities, we will look down the paths that we see as most important to capitalize on this work.

## II. Research Threads

### II.A. Point Gas Sensors (DARPA - MTO)

Driven by our own observations and the encouragement and support of ARO, in the mid 1990's we began to consider if the time had come for the development of the THz as a basis for gas sensors, analytical chemistry, and chemical intelligence. In 1998 we summarized these findings in a feature article in the 'A-pages' of the journal *Analytical Chemistry* of the American Chemical Society.<sup>1</sup> Shortly thereafter the program described here started and was used as a vehicle to transform these general observation into practical systems, with well defined characteristics relative to scenarios of interest. This work was funded via this ARO vehicle.

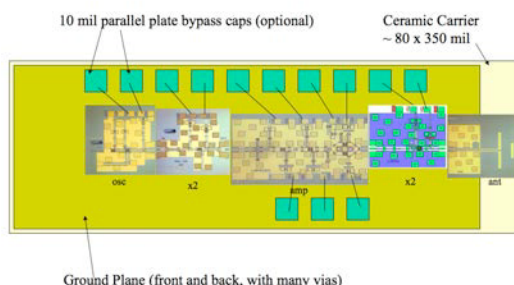


Figure II.A.1.1. HRL chip set for 330 GHz source.

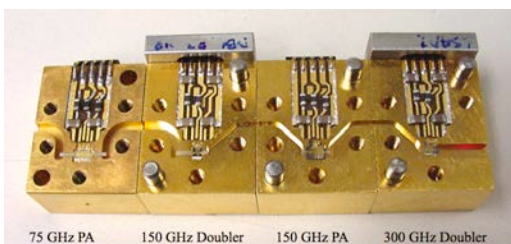


Figure II.A.1.2. HRL chips mounted in waveguide blocks (with upper half removed).

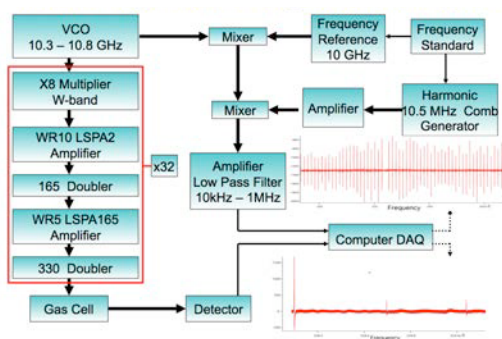


Figure II.A.1.3. Overview of the spectrometer system used with the HRL 330 GHz system.

#### II.A.1. The development and demonstration of the basic solid state THz gas sensor

The origins of this project were with a DARPA Program, THz Technology for Sensing and Satellite Communications, that provided the initial funding for the work reported here. All of the other elements of this Program were focused on THz technology development, primarily sources and detectors. Our role was to develop systems to utilize these and related technologies. In addition to testing and evaluating hardware that was to be developed as a part of the DARPA program, our focus became the development of a point gas sensor based on a program element led by Hughes Research Laboratory, with participation from JPL, MAYO, and UCLA. Their goal was to build an InP chip based transistor multiplier system that started with a VCO in the 80 GHz range and ended up with several milliwatts of tunable power around 330 GHz. Since this would be an ideal source for a sensor, we enthusiastically began working with them. The original strategy was that HRL would make the chips and MAYO would wire bond them together. Figure II.A.1.1 shows this concept.

However, it quickly emerged that the yield, reliability, and variable quality of the individual chips led to a low probability of success for the integrated module. We suggested that each of the chips be housed in its own waveguide structure so that it would be possible to mix and match successful circuit elements. We made these blocks, shipped them to the HRL team and after inserting the chips in the block, they were returned to us for testing and evaluation. Figure II.A.1.2 shows a set of these blocks.

Because the spectral purity of the integrated VCO was not sufficient for a high-resolution sensor, we replaced the VCO with one of our 80 GHz drivers, incorporated frequency scanning and measurement elements, and the system shown in Fig. II.A.1.3 resulted.

While this integrated approach is highly desirable for practical systems, the program ended before HRL could produce chips of sufficient bandwidth and power for a good demonstration of the potential of the SMM for gas sensors. {We note that DARPA has a new program (Terahertz Electronics) that continues down this transistor amplifier path, with goals of systems at 650 GHz, 850 GHz, and 1.03 THz.} Accordingly, we carried out in parallel a development path based on the diode multiplier technology that was beginning to be made available by Virginia Diodes, Inc. (VDI). Figure II.A.1.4

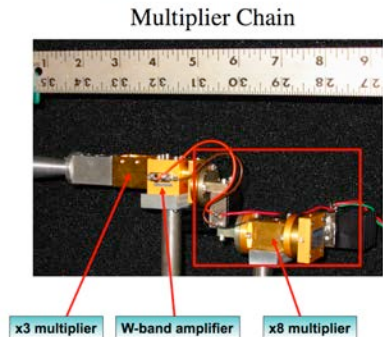


Figure II.A.1.4. VDI multiplier chain for 220 – 330 GHz.

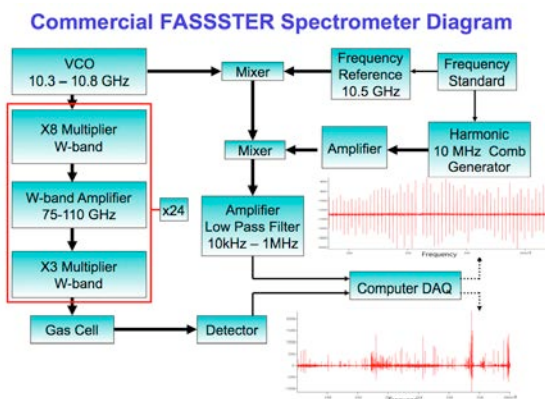


Figure II.A.1.5. Overview of the spectrometer system used with the VDI 330 GHz system.

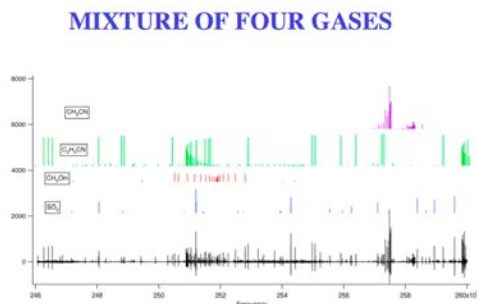


Figure II.A.1.6. Identification in a mixture of 4 gases.

shows the VDI multiplier chain and transmit horn. Figure II.A.1.5 shows it imbedded in the same spectrometer system as the HRL source. While simple, this was a highly successful system. Figure II.A.1.6 shows an analytical application based on a mixture of 4 gases.<sup>2,3</sup>

In this same time period there was considerable investment and effort devoted to the development of point gas sensors based on THz-TDS methods. During this period we were also attempting to interest potential sponsors in this work, and we were often asked to compare our approach with a variety of alternatives. Since the papers, web sites, press releases, etc. that described the THz-TDS work never made a comparison with the cw electronic techniques that we had developed, we felt that we needed to do so. In addition, the THz-TDS publications promulgated erroneous fundamental objections to cw systems: (1) cw system in the THz were 'plagued by noise', and (2) a 'dynamic range' of  $10^9$  for THz-TDS systems implied superior sensitivity. In the end, we felt compelled to write two papers:

1. F. C. De Lucia, "Noise, detectors, and submillimeter-terahertz system performance in nonambient environments," JOSA B **21**, 1273-1297 (2004).<sup>4</sup>
2. Medvedev, M. Behnke, and F. C. De Lucia, "Fast analysis of gases in the submillimeter/terahertz with "absolute" specificity," Appl. Phys. Lett. 86, 154105 (2005).<sup>2</sup>

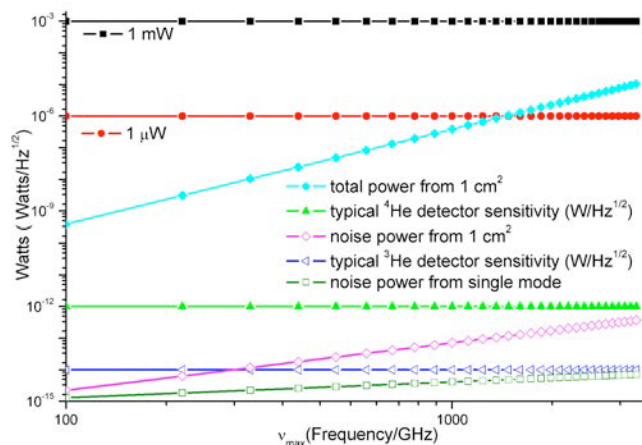


Figure II.A.7 Comparison of noise power and power in the THz as a function of the maximum frequency of the detector.

The first dealt with the issue of noise in cw systems. To briefly summarize, the idea that cw systems are 'plagued by noise' is based on (1) an error of about  $10^8$  which confuses thermal power with thermal noise, and (2) a misunderstanding of about  $10^4$  based on a lack of understanding of the single mode antenna theorem. Figure II.A.7 summarizes these results.

Since it was never explained how the ' $10^9$ ' dynamic range related to system sensitivity, we simply made a comparison between the performance of the very simple system shown in Fig. II.A.1.5 and the best THz-TDS sensor that

had been described in the literature (below we will describe a much better cw SMM system that makes the following comparison even starker). Briefly put:

- (1) The cw system is  $\sim 10^7$  more sensitive than the THz-TDS system in terms of ppx and  $\sim 10^{10}$  in terms of minimum detectable sample.
- (2) The cw system has about  $10^4$  more resolution.
- (3) This comparison is for a detection in the time domain which for the special case chosen for the THz-TDS made it possible for all of the signals from the many J and K populated levels to sit on top of each other and add. It would appear that the  $10^9$  'dynamic range' included all power at all frequencies (what really matters is only the power at a frequency that interacts with the molecular transition), and does not take into account that the spectroscopic problem of detecting a small change in a large signal is different than detecting a small signal (the radar or communications problem). This is a many orders of magnitude effect (depending upon circumstances, remember that a 100 W light bulb has far greater 'dynamic range' than  $10^9$ ). It ignores (among other things) Townes noise (a factor of  $\sim 10^8$ ) in typical systems.<sup>5</sup> This is the reason that spectra taken with THz-TDS systems rarely have spectral S/N much bigger than 100, even with substantial observation times. Figure II.A.1.8 summarizes these results.

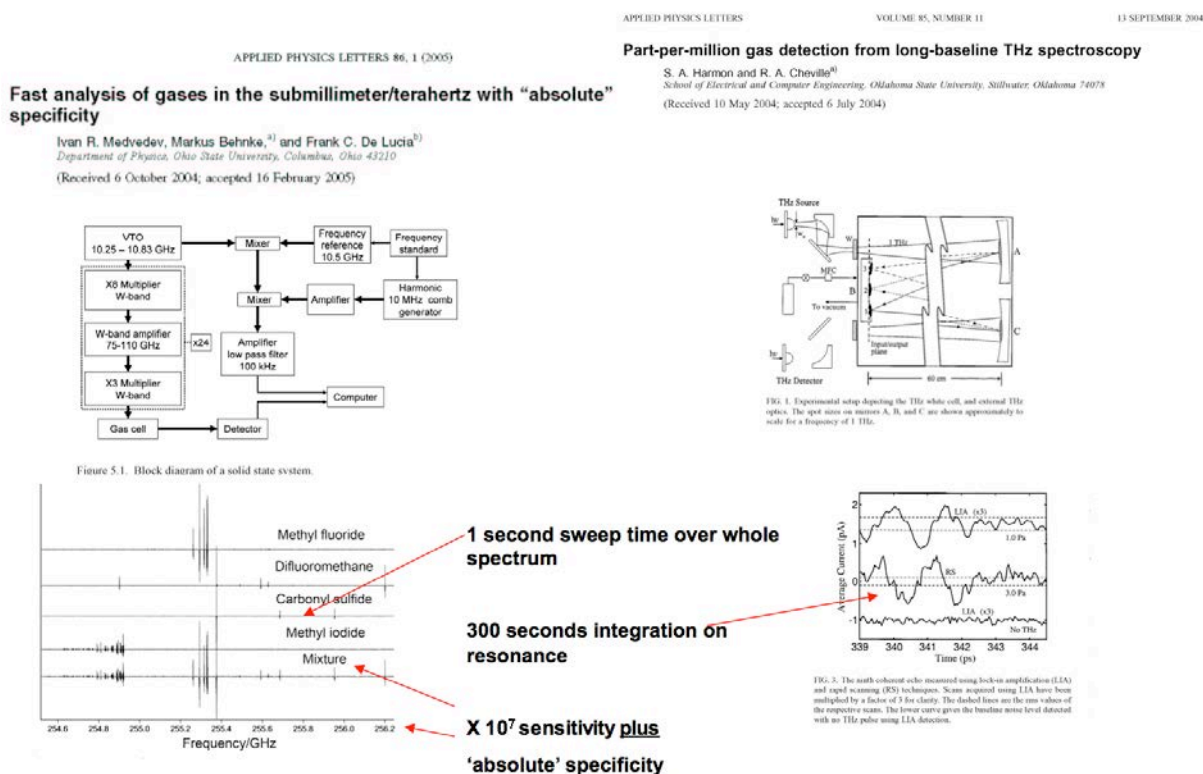


Figure II.A.1.8. A summary of the comparison of a cw submillimeter electronic gas sensor and the THz-TDS based gas sensor.

In the context of **DARPATECH 2004**, this work was highlighted as a part of their presentation as:

*"One such opportunity is the identification of chemical threats. Low-pressure gases have astonishingly selective signatures in this region. In MTO's recently completed Terahertz Technology for Sensing and Satellite Communications program, a relatively compact chemical sensor was developed and shown to have incredible absolute specificity even when dealing with very complicated mixtures. Further advances could lead to very inexpensive and portable systems."*



## II.A.2 Specificity: Scenarios and Clutter (DARPA – STO)

The next step in the development of the point sensor project was to answer a series of questions, primarily from DARPA, related to the specificity of this approach, especially in cluttered atmospheres and scenarios. While many of these results were not surprising to an experienced SMM spectroscopist, given the amount of snake oil for sale in the THz we understood the need for demonstrations. In the end we came to understand that the results were even more favorable than we had imagined, we understood why, and we have been able to develop system strategies to take advantage of the underlying physics.

In the first of the requested demonstrations, we were to prepare 30 gases, of which 20 would be selected blindly by a representative of DARPA from WPAFB to be placed in a mixture in our spectrometer. We were then to record the spectrum of the mixture and identify the components of the mixture. Figure II.A.2.1 shows the results on a highly compressed scale.

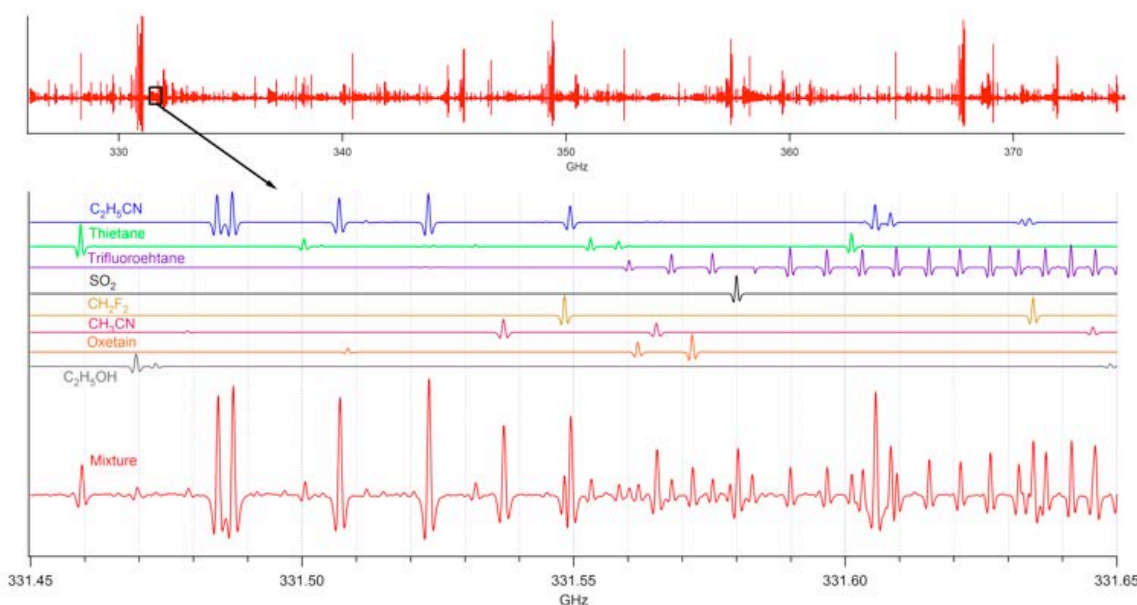


Figure II.A.2.1. Spectrum of a mixture of 20 gases on a highly compressed scale (upper panel). The lower panel shows an expansion of a small portion of the spectrum for the identification of 8 of the gases (middle panel). Many such regions exist and collectively they provide ‘absolute’ specificity for all of the 20 gases.

The identification of the 20 gases in the mixture was done by first identifying a fingerprint region for each of the 30 gases, followed by ‘visual’ identification. One of the 20 identifications is shown in Fig. II.A.2.2. In fact,

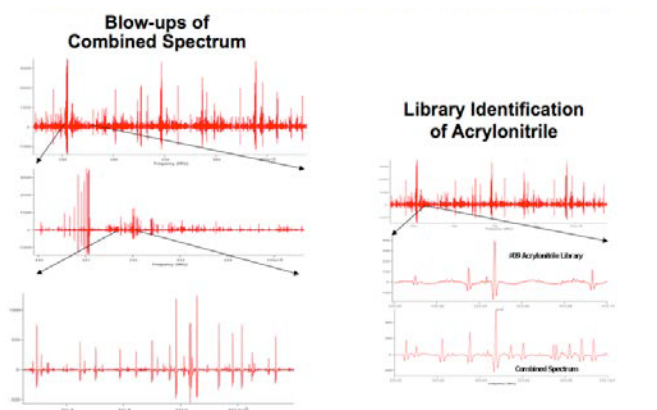


Figure II.A.2.2. Visual identification of one of the 20 gases in the mixture.

many such regions exist for most gases. A numerical identification algorithm, based on a simple threshold model, showed that the probability for false alarm (PFA) for the least favorable of the gases in the mixture was  $10^{-107}$ , thus justifying our use of the term ‘absolute’ specificity.

After this successful demonstration, DARPA became concerned that atmospheric background clutter would be problem. In response, we first used the literature. Table II.A.2.1 shows the constituents of both a clean and a polluted atmosphere. This table shows what might be called the ‘miracle of the submillimeter’. In order of concentration, these gases have either no spectrum ( $N_2$ , Ar,  $CO_2$ , Ne, He,

**Table II.A.2.1 (ppb)**

Species	Clean Troposphere	Polluted Air
N <sub>2</sub>	780,840,000	780,840,000
O <sub>2</sub>	209,460,000	209,460,000
H <sub>2</sub> O	variable	variable
Ar	9,340,000	9,340,000
Ne	18,000	18,000
He	5200	5200
Kr	1100	1100
Xe	90	90
H <sub>2</sub>	580	580
CH <sub>4</sub>	1650	1650+
CO <sub>2</sub>	332000	332000+
N <sub>2</sub> O	330	330+
SO <sub>2</sub>	1 – 10	20 – 200
CO	120	1000 – 10000
NO	0.01 – 0.05	50 – 750
NO <sub>2</sub>	0.1 – 0.5	50 – 250
O <sub>3</sub>	20 – 80	100 – 500
HNO <sub>3</sub>	0.02– 0.3	3 – 50
NH <sub>3</sub>	1	10 – 25
H <sub>2</sub> CO	0.4	20 – 50
HCOOH		1 – 10
HNO <sub>2</sub>	0.001	1 – 8
CH <sub>3</sub> C(O)O <sub>2</sub> NO <sub>2</sub> (PAN)		5 – 35
Non-Methane Hydrocarbons		500 – 1200

<sup>1</sup>.Data from Seinfeld<sup>4</sup>

CH<sub>4</sub>, Kr, and Xe) or at Doppler resolution in the SMM extremely sparse spectra (H<sub>2</sub>O, O<sub>2</sub>, N<sub>2</sub>O, SO<sub>2</sub>, CO, NO, NO<sub>2</sub>, O<sub>3</sub>, NH<sub>3</sub>, and H<sub>2</sub>CO). Of the well-defined species this leaves HNO<sub>3</sub> at ~10 ppb in the polluted atmosphere and 0.1 ppb in the clean atmosphere as the first potential ‘clutter’ molecule. Even at that, HNO<sub>3</sub> (which we have studied extensively in our laboratory) has strong lines that occupy << 1% of the spectral space. In the polluted atmosphere, this leaves PAN (which is unstable and can be eliminated in the collection process) and the general category ‘non-methane hydrocarbons’. While a definitive statement would require a better definition of what these species are, we expect that this would contribute a general background of many very weak lines. Figure II.A.2.9 shows this result graphically, along with the lethal and impairment concentrations from a list of Toxic Industrial Chemicals (TICs).

DARPA decided that they would like to spend some money to get a better answer so they contracted with NOAA to provide us with sample mixtures representative of 6 locations around the world (from the south pole to NYC) for us to make direct clutter tests on. As one might expect, early in the project NOAA pointed out to DARPA that it was not possible to make these mixtures because unknown and unanticipated reactions in the mixture. At this point a sensible

thing was done. NOAA provided the samples individually, we recorded each spectrum separately, and then we synthesized the spectrum at each of the 6 NOAA locations according to the NOAA atmospheric measurements.

While the NOAA atmospheres differed in detail for the trace species, the overall results were the same. There is no clutter problem. One of the more interesting things that we have found is that the polluted atmospheres available from different sources reflect their interests. For example the NOAA atmospheres included many of the hydrofluoroclorocarbons because they have been major targets of regulation. The second thing that we learned is that it is actually quite hard to make these measurements, largely because many of the analytical techniques used are not that specific. For example the category ‘non-methane hydrocarbons’ is not the sum of many individual measurements

lumped into this category for display, but rather because the species are not separated into individual species by many measurement methods.

While it is possible to ask questions about an infinite number of scenarios, there is in fact a very simple and universal principle at work. Because of the ‘complex redundancy’ of the rotational fingerprint, as the concentration of the target gas is increased from zero at some concentration the identification statistics rapidly change from random (no specificity) to ‘absolute.’ This is because the probability of a false alarm is the probability of accidentally getting a seven digit match on a line frequency *raised to the power of the number of lines in the fingerprint*. If the algorithm takes into account that the relative intensities of the fingerprint lines are known, the statistics become even more favorable.

This means that the questions of importance are: (1) what concentration is required to detect the spectral lines, and (2) does the species in question have a high resolution spectrum (the large molecule limit)?

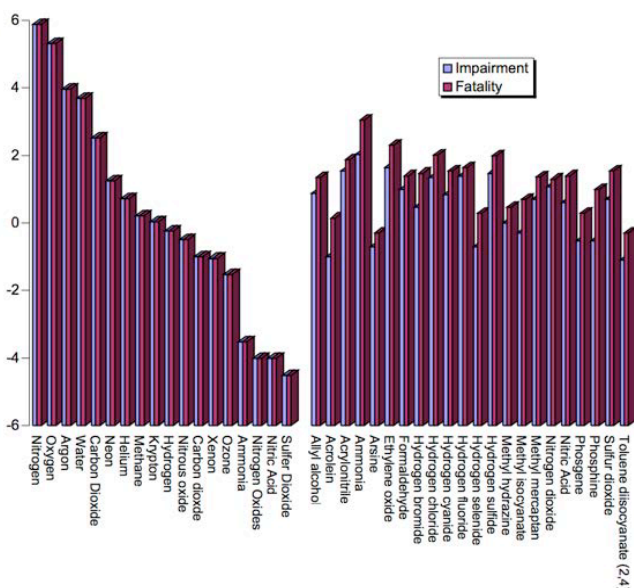


Figure II.A.2.9. Concentration of atmospheric gases in comparison to the fatal and impairment concentrations of TICs).



## II.B Remote Spectroscopic Sensors (DARPA – STO)

The sensors described in Section II.A are ‘point’ sensors, which draw an atmospheric sample into the sensor for analysis. There are many applications in which you would like to do this remotely. However, this is a much harder challenge. Spectroscopically, the issue is pressure broadening. In the sensors described above, the pressure of the sample is reduced by  $\sim 10^5$  and it is this low pressure (combined with the small Doppler limit in the SMM which makes this low pressure useful) that makes the SMM so favorable.

A number of years ago, we were encouraged by ARO to ‘think hard’ about this problem to see if there were any new and creative approaches. While there have been many line narrowing techniques developed over the years (e. g. Dicke narrowing, Lamb dips, etc.) we concluded on rather fundamental grounds that since atmospheric broadening resulted from collisions interrupting the wavefunction that described the state that this uncertainly principle limit on linewidth would always be a limit in the atmosphere. Therefore, we needed a way to transcend this limit rather than to eliminate it.

First, we need to realize that there are two issues. The impact of the line broadening on specificity is widely recognized. However, the second is not and is usually ignored in proposals for the use of the SMM for remote spectroscopic sensing. More specifically, one of the things that is fundamental to the sensitivity of SMM spectroscopy in general and SMM point sensors specifically is that the narrow Doppler limited lines are easy to separate from broader system power fluctuations which arise from standing waves, impedance mismatches, etc.). With narrow lines it is possible with modest integration times to observe lines that absorb  $10^{-7}$  of the probe power. However, power variations on the order of an atmospherically broadened spectral line are typically  $>10^{-1}$ . Absent a means of separating the molecular absorptions from the system instrument function, systems will loose  $10^6$  in detectivity.

This latter challenge is illustrated by a DoE experiment at their Nevada Test Site. In this experiment they released a rather large concentration (145 ppm) of a favorable molecule (methyl chloride) into a 4 m atmospheric path and attempted to detect the *single* gas. Figure II.B.1 shows the result.

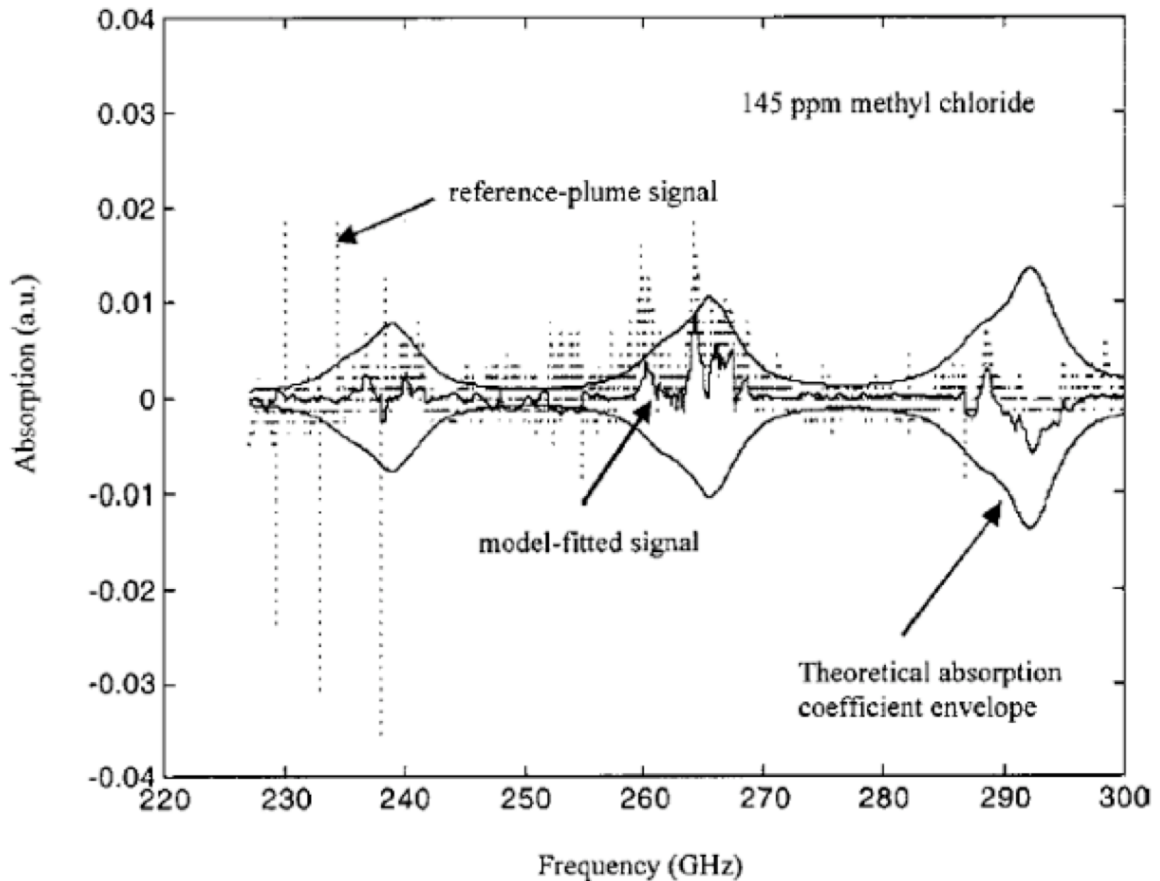


Figure II.B.1. Results of an air release of 145 ppm of methyl chloride in a 4 m atmospheric path.

The solid line in this figure is a calculation of the expected pressure broadened absorption (drawn as an envelope to allow both positive and negative(?) absorption). The dots represent the result of individual scans and the solid scan are the averages of 40 such individual scans. There is no physics associated with the ‘signature’ in the experimental results. Rather the trace results from fluctuations (largely in the atmospheric path) and standing waves. The ‘detection’ is accomplished by comparing the frequency locations of this noise with the expected locations of the molecular absorptions, as indicated by the aforementioned envelope.

Figure II.B.2 shows a proposed solution to this long-standing problem. To summarize the science briefly:

- (1) The time resolved pump makes it efficient to separate signal from atmospheric and system clutter, thereby gaining a large factor in sensitivity (Thus eliminating the fluctuation problems shown in Fig. II.B.1.)
- (2) The 3-D information matrix (pump laser frequency, probe frequency, and time resolved molecular relaxation) can provide orders of magnitude greater specificity than a sensor that uses only one of these three (for example the frequency axis of Fig. II.B.1).
- (3) The infrared pump frequency must correspond to molecular absorption frequencies, but ~all millimeter probe frequencies correspond to rotational transitions => the probe frequency selection is driven by other scenario dependent trades (e.g. atmospheric transmission).
- (4) The congested and relatively weak spectra associated with large molecules can actually be a positive because the usually negative impact of overlapping spectra can be used to increase signal strength.

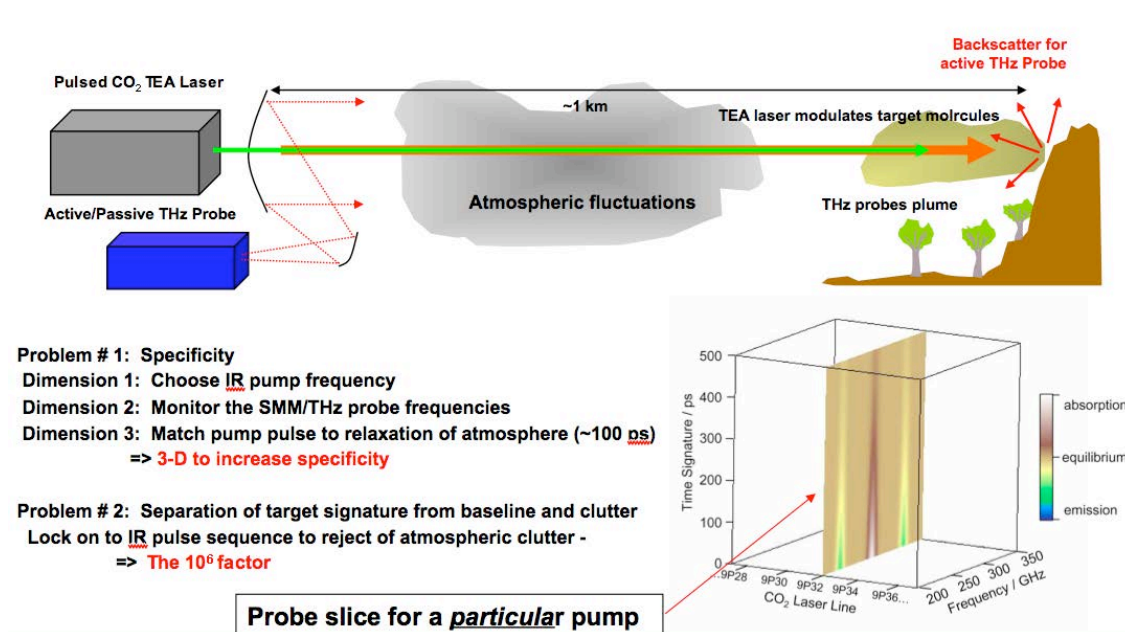


Figure II.B.2 Double resonance scheme for remote chemical sensing in the atmosphere.

Although we worked on this for more than a decade, until recently we did not push for agency support to further develop or test the concept. While the high pump intensity – fast pulse regime would have given us the opportunity to explore new science (e. g. is there continuum – continuum coupling between the IR pump and the THz probe, and if so, what of the many models and explanations for these continua are consistent with the experimental results), it seemed to us that the required supporting technology was too far away for us to try to sell this as a sensor. However, a few years ago technical development, most notably the availability of a compact solid state THz technology, significantly changed this and we sought to start a laboratory project to address the most significant scientific uncertainties:

- a) Possible cross coupling clutter at high pressure (the continua – continua coupling).
- b) The nature of molecular relaxation at high pressure
- c) The spectroscopy of large molecules at high pressure

These are being considered in a new DARPA Seedling which is described in Section III.

## II.C. Imaging (DARPA TIFT)

For many years there has been a considerable interest in the use of this spectral region for imaging. Briefly put, much of this interest is because the SMM/THz represents a useful compromise between imaging resolution and atmospheric/obscurant penetration.<sup>6-11</sup> In the context of the penetration of fog and other precipitation it led to the Army's Near Millimeter Wave program of the 70's. More recently the focus has been on the penetration of clothes, packaging, etc. for the detection of weapons, explosive, and drugs. It was largely in this latter context that the DARPA TIFT program was started and it is our participation in this program that was funded via this contract.

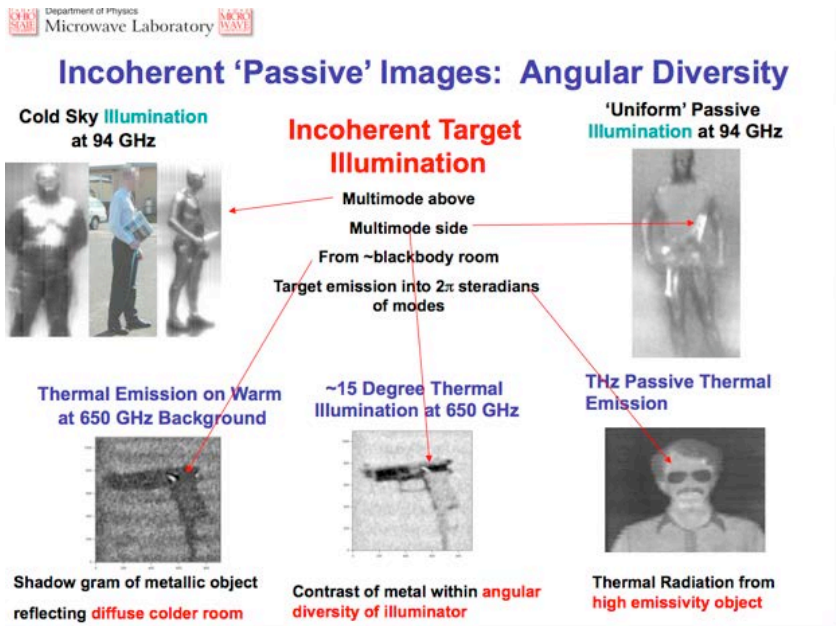


Fig. II.C.1. Summary of some passive imaging phenomenology.

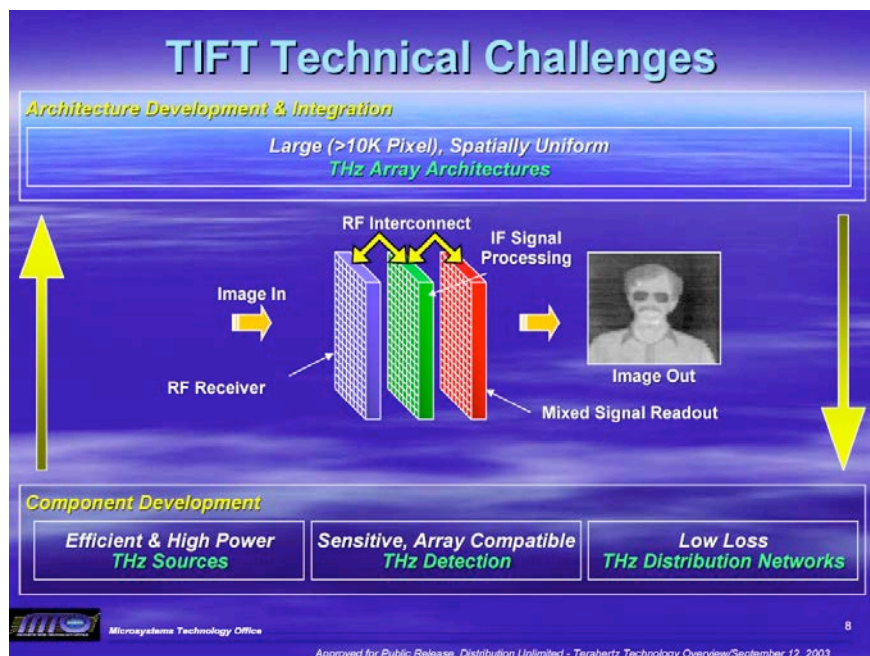


Figure II.C.2 DARPA use of passive image.

Early on, we made several observations that had an impact on the decision to focus the TIFT program primarily on active rather than passive systems. Some of these results are summarized in a viewgraph that we reproduce here as Fig. II.C.1. The first observation is that most of the 'THz' passive images had been made at 0.094 THz *outside*. As shown in the upper left image in this figure, this allowed the cold sky illumination (the atmosphere is relatively transparent at 94 GHz to cold space) to provide a large contrast for the radiometer. This contrast is not available in the THz because the atmosphere is not transparent to cold space, nor is it available indoors.

The second observation is that the objects of interest were typically oriented to provide a specular reflection from the cold sky illumination into the radiometer. This is seen in both the upper left image and the upper right image, which used a cold illuminator. The image in the lower left shows a contrast between a warmer background (e. g. a body) and a colder room. Since the room is essentially a blackbody that fills all illumination modes with the same temperature, the target is seen as a shadow gram. The image in the lower middle was made with a cold illuminator and depending upon whether the target reflected the room, the cold illuminator, or some combination, additional detail is observable. The image at the lower right is a pure thermal emission picture that we made



many years ago with a very good  $^3\text{He}$  bolometer centered on  $\sim 700$  GHz. This has been a rather successful image and has been used for a number of purposes, including the ‘selling’ of the TIFT program, as shown in Fig. II.C.2. A more detailed report of this work has been published<sup>12</sup> and we expect that another paper that focuses on the impact of obscuration will be published as well.

Active images are very different from passive images. Figure II.C.3 shows a comparison. The most notable feature is that active images are dominated by specular reflections (see the parts of the face that are perpendicular to the illumination of the

active imager) and scatter from features similar in wavelength to the illumination (see the beard). On the other hand, the passive imager simply measures temperature independent of angle. This is because the blackbody radiation fills the many modes of the full  $2\pi$  steradians.

An image of a target can serve to illustrate the impact of specular reflections. Figure II.C.4 shows a 650 GHz active image of a carefully posed gun, with and without the obstruction of a heavy lined ‘Middle Eastern’ robe. Although the robe provides some clutter, the return image of the gun is strong and easy to identify.

This raises the issue of what happens if the gun is not carefully posed. Figure II.C.5 shows the same gun with a small rotation both on a log and linear scale. Even the small rotation largely makes the gun disappear. However, we were able to show that because of the large dynamic range of active imaging that log processing in the IF of the heterodyne receiver produced a good image, without the need for perfect alignment. This is illustrated in Fig. II.C.5 by the difference between the log and linear images.

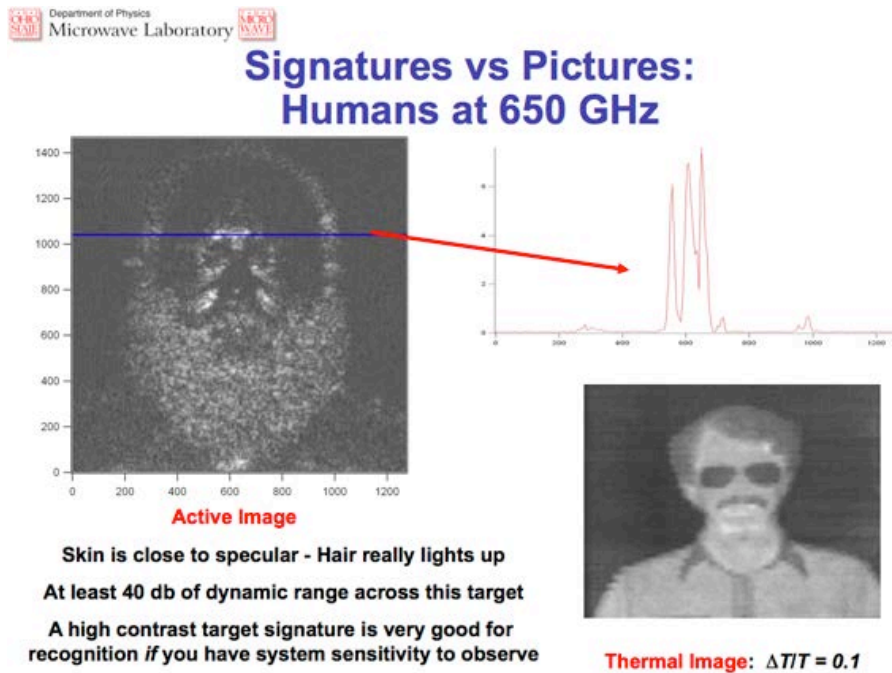


Figure II.C.3 A comparison of active and passive images.

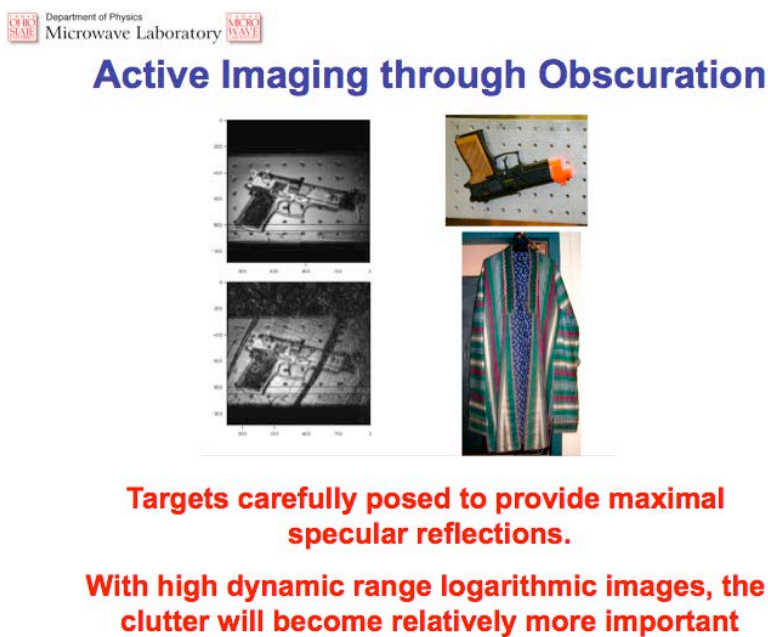


Figure II.C.4. 650 GHz of carefully posed gun.

## Target on Log and Linear Scales

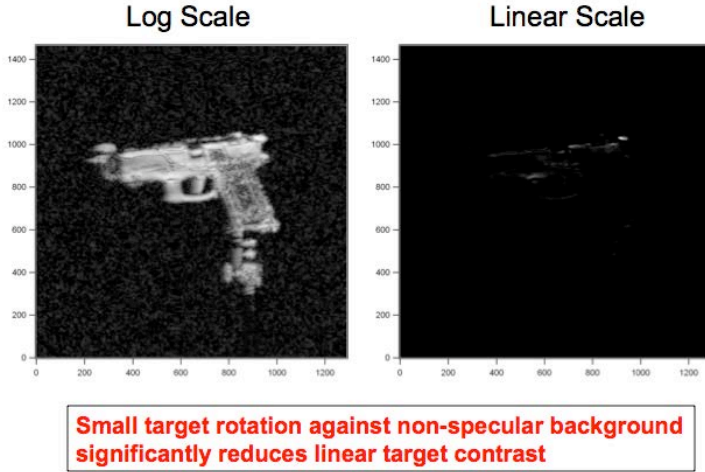


Figure II.C.5. Slightly rotated gun on log and linear scales.

## Multimode illumination - Preliminary results

Can we use active illumination to make very hot 'passive' pictures?  
i.e. remove the need for special angles

1 mW in 100 Hz in a single mode corresponds to a temperature of  $10^{18}$  K  
For a 'room/canyon' of scale  $l = 100$  m, with 'wall' reflectivity  $R_w = 0.1$  and target reflectivity  $R_o = 0.1$ ,

$$T_o = 10^{18} K \left( \frac{\lambda}{l} \right)^2 R_w R_o \sim 2.5 \times 10^7 K$$

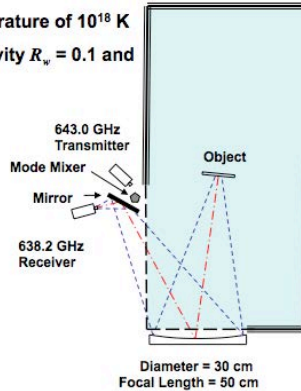


Figure II.C.6. Multimode illumination chamber.

This is the good news, the bad news can be seen in Figure II.C.4: There is considerable backscatter from the obscuring robe and no matter how sensitive the imaging system and how clever the IF signal processing, the much weaker signal from the rotated gun is obscured by the robe backscatter. While we do not have space to describe it here, we were able to show that this clutter is largely from coherent effects and very small rotations (or alternatively, multimode illumination) greatly reduces this effect.

Accordingly, we built a multimode illumination chamber, shown in Fig. II.C.6 to test this idea and the preliminary results are shown in Fig. II.C.7. The key idea here is that in a single mode with a 100 Hz bandwidth detector, 1 mW of power corresponds to  $10^{18}$  K. If we assume a room or an 'urban canyon' of scale size 100 m and illuminate all of the modes in the 'blackbody', this corresponds to a temperature over  $10^7$  K. This would appear to be a simple and practical method for eliminating the problems associated with special angles and well-posed demonstrations in active illumination systems and to return to the 'no special angles' associated with passive imaging. Additionally, we were able to demonstrate mode-mixing schemes to eliminate or reduce the coherent problems associated with active imaging. The end goal of this is to have an image that is equivalent to passive illumination at a tem-

perature of  $10^7$  K. Active imaging also makes possible time of flight (radar like) ranging.

Figure II.C.7 shows the preliminary results. Because all of the modes are illuminated more or less equally, the target, as shown in the upper left, provides little contrast because of the coherent interaction among the modes. In passive imaging, there is no coherence among the modes in a blackbody. However, the introduction of mode mixing largely eliminates this problem as shown in the middle figure. Additionally, the scale of the remaining coherent speckle (which could also be eliminated by modulating the frequency/phase of the illuminator) is considerably smaller than the scale of the diffraction limited image. Thus it is possible to average away much of the speckle without degrading the resolution of the image.

## Multimode Illumination Results

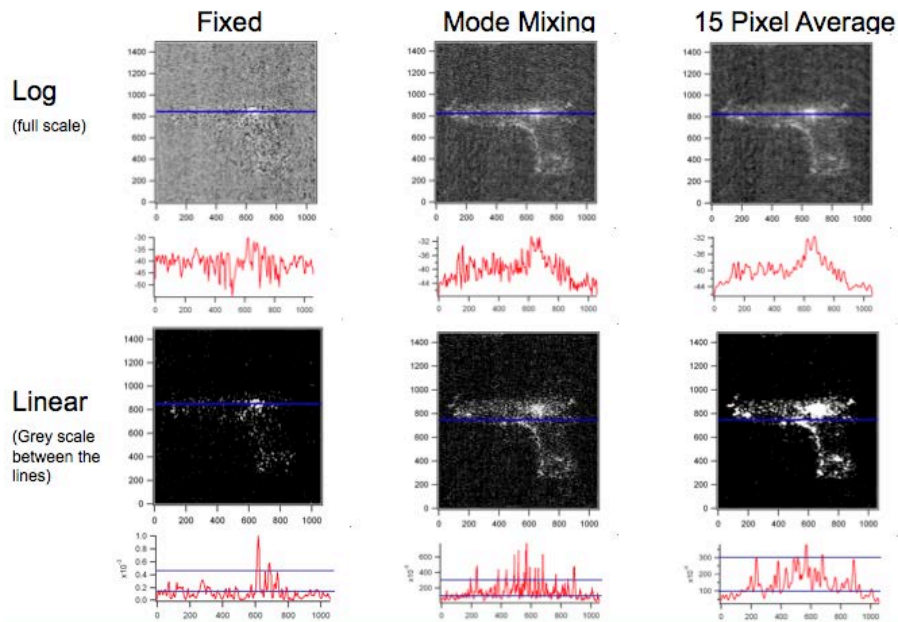


Figure II.C.7. Preliminary results from multimode illumination.

## Brown robe, Log images

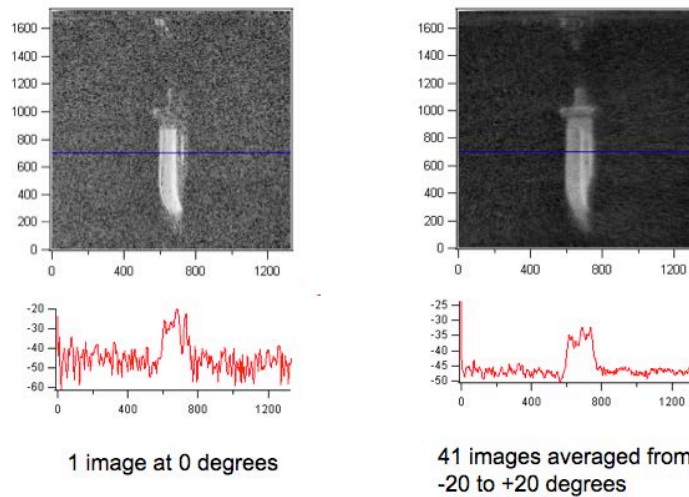
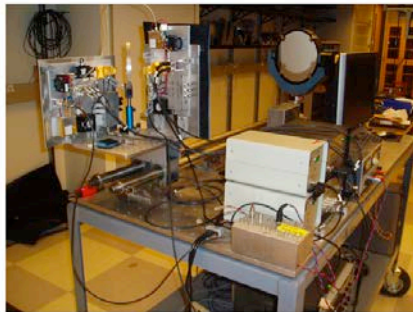


Figure II.C.8. A comparison between single mode illumination at the optimum angle (left) and multimode illumination from many angles (right).

## Portable 650 GHz Imaging System



### Indoor and outdoor high dynamic range images under 'typical' conditions

**What are impacts of multiple reflections in real images?**

**What are distance and atmospheric limits?**

Figure II.C.9. Portable 650 GHz active imaging system with 60 cm rapid scan objective mirror.

Figure II.C.8 shows how multimode (or equivalently, multiangle) illumination can be used to significantly reduce the clutter from a robe covering a knife. This figure shows that the multimode illumination that includes mostly 'non-optimum' angles is significantly better than single mode illumination, even when that single mode is optimally angled.

Figure II.C.9 shows the 650 GHz portable imager mounted on a rolling table. This system has a rapid scanning 60 cm objective mirror. It was the intention of using this in Phase II TIFT to make observations are ranges of tactical interest and to further investigate the concepts discussed above. However, TIFT ended with Phase 1B.

Finally, because there has been so much discussion of using 'THz' radiation to 'see through walls' (including a recent Army SBIR), we show in Fig. II.C.10, measurements ranging from 0.1 THz to 0.5 THz of the transmission through common building materials. Since most common building materials have a loss (one way) of  $\sim 50$  db at 0.55 THz, we conclude that if one wants to see through walls, that it is best to look in houses built of foam or to work at frequencies that are a small fraction of 1 THz.

Figure II.C.11 shows our conclusions at the end of TIFT Phase 1B.



## Building Materials

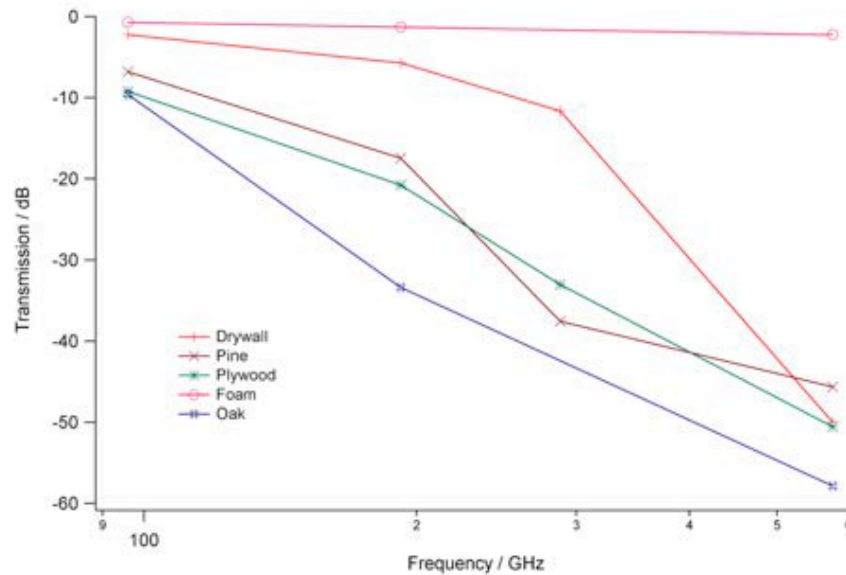


Figure II.C.10. Attenuation (one way) through common building materials from 0.1 to 0.55 THz.

## Conclusions

1. In **passive** imaging, the thermal emission from the target and the reflected 'passive' thermal illumination are both multimode.
  - a. No special angles for strong specular reflections
  - b. A relatively low contrast:  $\Delta T/T$  - but no speckle modulation
  - c. Off axis(bistatic) thermal illumination improves this contrast (true for active as well)
2. in **active** imaging, there are many possible illumination strategies
  - a. Monostatic systems results in glints from corners and normal surfaces which are many orders of magnitude stronger than returns from non-normal or scattering surfaces - signatures?
  - b. Logarithmic processing recovers this range of data and can provide images with significantly enhance recognition
  - c. 'All' mode illumination closely resembles passive imaging IF the coherence among the illumination modes is destroyed
3. **Obscurements:** Active systems can have very large system S/N. However, the clutter associated with covering obscurements can limit a system long before the system S/N
  - a. Much of this clutter is coherent, and multimode approaches can significantly reduce/eliminate it
  - b. Recognition strategies based on the strong glints rather than images
4. **Range:** Because spot size is a function of range, the definition of normal is a strong function of range (i.e. active illumination will be a complex function of range, not just a diffraction degradation)

**Models which describe and compare system approaches must reflect these target and range effects as a function of illumination strategy**

Figure II.C.11. Conclusions for the Phase IB TIFT program.



## II.D Multimode approaches to the separation of broad resonances from clutter (Navy)

There has been considerable interest in the use of the THz for spectroscopic sensing of solids and high-pressure gases. However, all of these applications are made challenging because the broad spectral resonances of these targets are hard to separate from system variations (standing waves). This is mostly a result of the use of the usual 1-D (line of sight) sensing geometry because the density of standing wave states in 1-D is similar to many spectral signatures in width. This makes such sensing orders of magnitude more difficult than the sensing of low-pressure gases (their narrow lines can be effectively used to discriminate between target spectral signatures and system variations). However, in 3-D the density of states is much denser than in 1-D. If it were possible to develop multimode sensors and to average over these modes, this problem might be eliminated or at least greatly reduced.

The spectroscopic basis of one attractive application - the sensing of hydrogen peroxide in the atmospheric

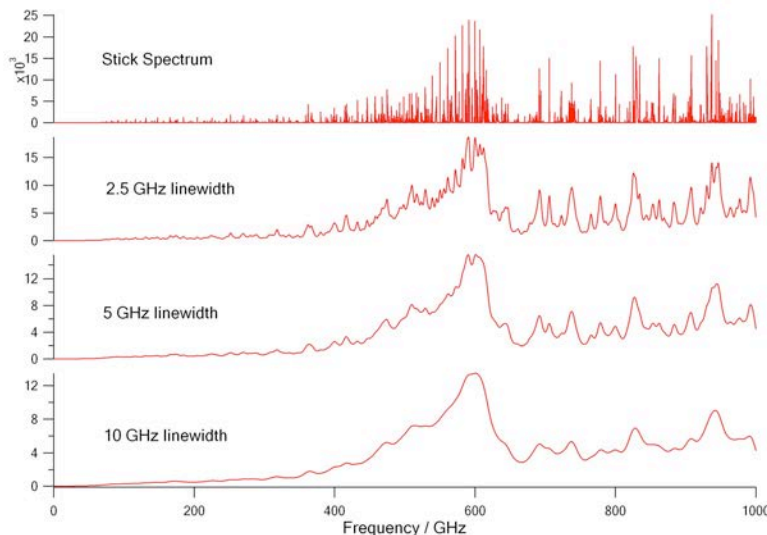


Figure II.D.1. THz spectrum of hydrogen peroxide as a function of linewidth.

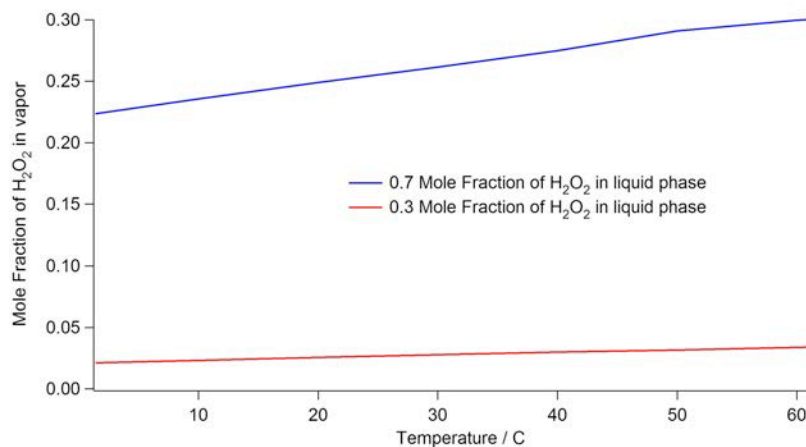


Figure II.D.2. Vapor pressure of hydrogen peroxide as a function of mole fraction in a water solution.

pressure headspace of a bottle - is shown in Fig. II.D.1. While many of the signatures of other targets of interest are of molecules whose spectra at atmospheric pressure are essentially continua, hydrogen peroxide is an exception. Based on our earlier work on this species, we have simulated in Fig. II.D.1 its spectrum at various linewidths (the 5 GHz spectrum shown in the figure is a good approximation of its signature at atmospheric pressure). The significant result shown here is that a detailed fingerprint for hydrogen peroxide at atmospheric pressure exists *if it is possible to separate this signature from system variations*.

Some the findings from our work were positive with respect to using SMM radiation to investigate the head-space of bottles for the presence of hydrogen peroxide and some less so. Let's start with the negatives:

1. Figure II.D.2 plots the results of thermodynamical calculations that show the amount of *gas phase* hydrogen peroxide as function of the hydrogen peroxide concentration in the *liquid*. This shows that the fraction of hydrogen peroxide in the gas phase is *considerably less* than in the liquid for reasonable liquid concentrations. We could get better results by working with higher concentrations of liquid hydrogen peroxide, but it seems to us that

these higher concentrations would represent unreasonably favorable scenarios.

2. Figure II.D.3 shows an overview of the absorption of the gas phase sample above the liquid as a function of pressure. One of the consequences of '1' is that at high pressure (~atmospheric) the water line at 557 GHz has a strong shoulder in the regions where we would like to sense the hydrogen peroxide.

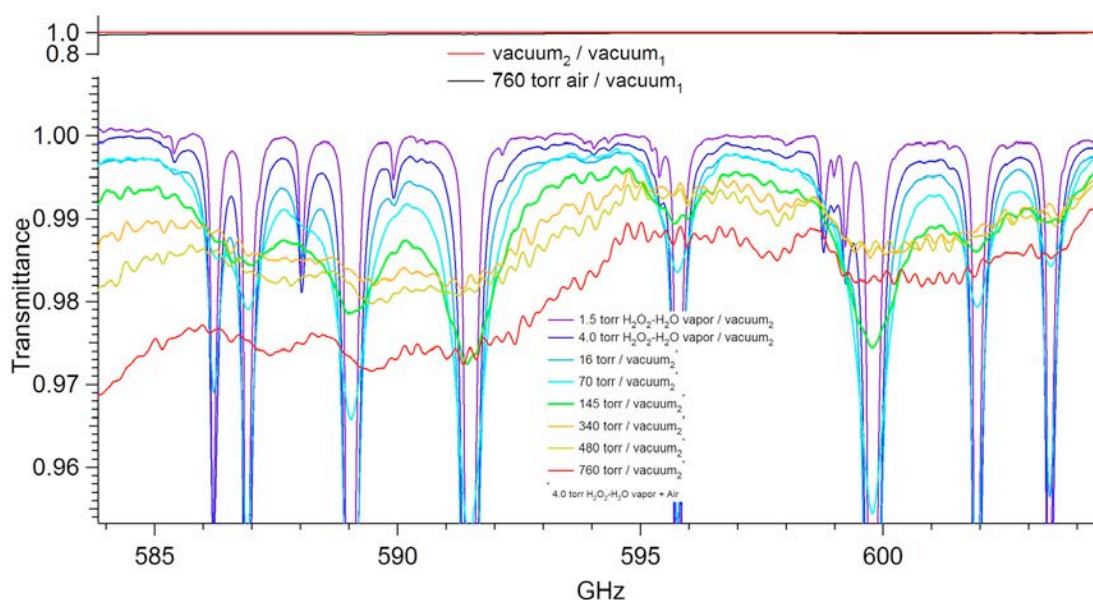


Figure II.D.3. Spectrum of mixtures of water and hydrogen peroxide at different pressures.

Figure II.D.4, which shows more detail around a cluster of hydrogen peroxide lines, shows more encouraging results. More specifically:

1. There is no noise in any of these graphs - all of the 'features' are real. At low pressure, you see a number of weaker lines, but at higher pressure you see interference/overlap effects among the lines.
2. For the higher pressures you see the hydrogen peroxide lines shrink in amplitude, but broaden - an expected effect.
3. These figures were made using 1 - D averaging to reduce the standing wave effects on the baseline. As we had hoped, this was effective.
4. This figure also displays a theoretical model of the expected pressure broadened spectra of the mixture. The good agreement between the theory and the experiment shows that a numerical retrieval of the hydrogen peroxide concentration could be effective.

Our conclusions:

1. The thermodynamics that reduce the concentration of hydrogen peroxide in the vapor reduce the effectiveness of this approach, but do not preclude it.
2. As shown in the lower panel of Fig. II.D.4, while the extra absorption associated with the shoulder of the water wing makes the visual impact of the hydrogen peroxide lines smaller, we understand the theory of water pressure broadening very well and should be able to deal with it numerically.
3. The 1 - D averaging was successful. A 2 - D scheme, should further improve these results.
4. We feel that in real world scenarios that the application of this approach would be challenging, however probably no more so than the spectroscopic detection of explosives in the THz.

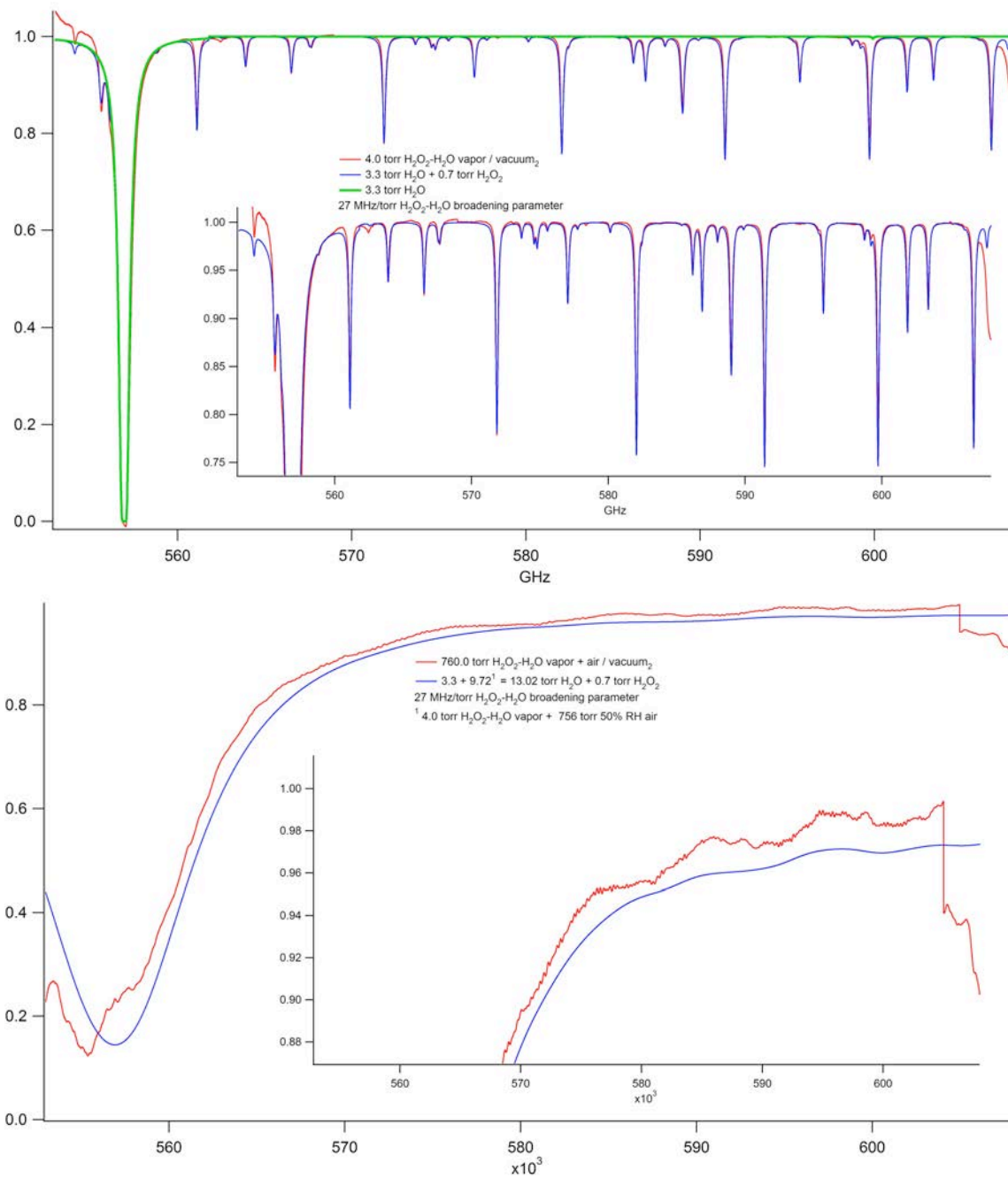


Figure II.D.4 Mixture of hydrogen peroxide and water at a total pressure of 4 Torr (upper panel) and at 760 Torr (lower panel). 1-D averaging has been used to reduce the standing wave phenomena.

## II.E Rydberg Photocathodes for the THz (TIFT/Navy)

The purpose of the TIFT program was to develop a focal plane array for THz imaging. One of its main challenges was the development of a technology that was scalable to an  $\sim 100 \times 100$  array. During the TIFT program we proposed a non-electronic alternative, the use of Rydberg atoms in a system analogous to that currently used for the highly successful night vision technology. This was done in collaboration with Professor Douglas Schumacher of Ohio State University, who is an expert in Rydberg atoms and who provide most of the insight, as well as the detail calculation describe below.

The fundamental problem that we address is that all photocathodes have a wavelength cutoff related to the work function of the photocathode material. While advances have been made in extending this cutoff toward the THz, if we restrict our definition of the THz to frequencies for which we have atmospheric transmission and some reasonable penetrability of obscurants ( $<1$  THz), the state of the art is still far from this frequency. Moreover, since 1 THz corresponds to  $1/6 kT$ , it is easy to argue on fundamental grounds that photocathodes at or near room temperature

will *never* be achieved at 1 THz. This is the reason that imaging at long wavelength has focused on ‘electronic’ rather than ‘quantum’ approaches.

It appears that a technologically useful solution exists which would use so-called Rydberg atoms. A conceptual overview is shown in Fig. II.E.1. In this approach, a low level ( $\sim 1$  mW) source is used to illuminate the target. The sensor is identical to the usual ‘night vision’ sensor, expect that the focal plane is proved by Rydberg atoms.

As shown in Fig. II.E.2, a gas of atoms is pumped to a highly excited state, called a

Rydberg state, by a compact solid state laser such that radiation in the THz range is able to effectively drive transitions to neighboring states. The population in the neighboring states is the detected signal. The ‘miracle’ of this approach is that simple field ionization can trade an atom in the  $18f$  state for an electron, without ionizing the atom in the lower  $20d$  state. The ‘physics’ of this is that whereas in a normal photocathode selectivity is related to  $kT$  (which is much larger than a THz photon), in the Rydberg case the selectivity is based on quantum mechanical selection rules, thus transcending the  $kT$  limitation. We have considered this approach in some detail, including the specifics of the required pump lasers, gas densities, etc. and it appears that a quantum efficiency for this photocathode of 10% is possible.

A schematic of the proposed system is shown in Fig. II.E.3. As can be seen, it shares much in common with standard night vision technology, perhaps most importantly in that it does not require complex readout strategies and interconnects because of its direct transition from optics to electronics via the microchannel plates.

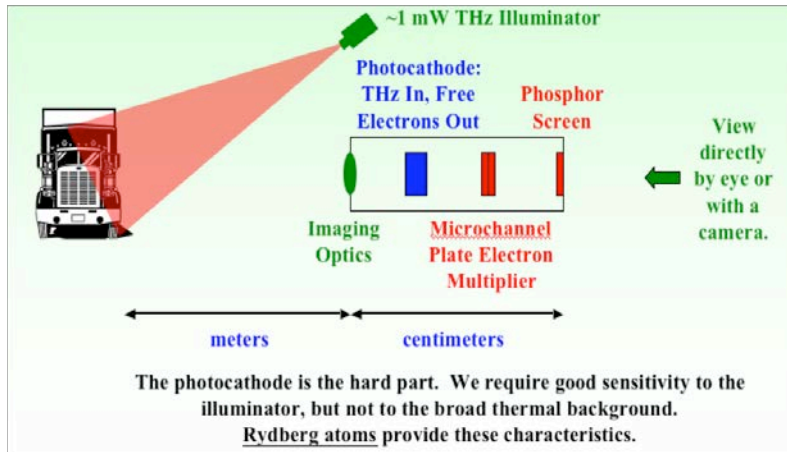


Figure II.E.1 Conceptual THz imager based on ‘night vision’ approach, with Rydberg atoms forming the photon to electron converter in the focal plane.

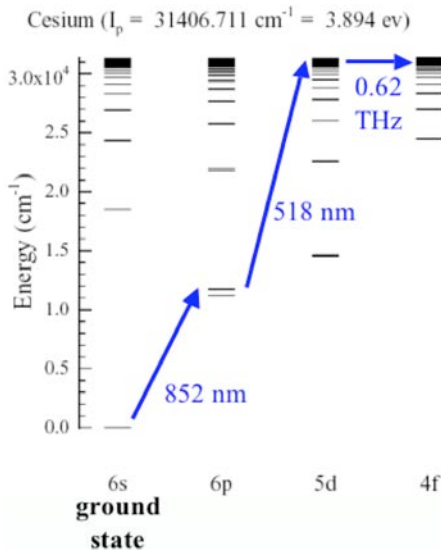


Figure II.E.2 Energy levels associated with the Rydberg Photocathode.

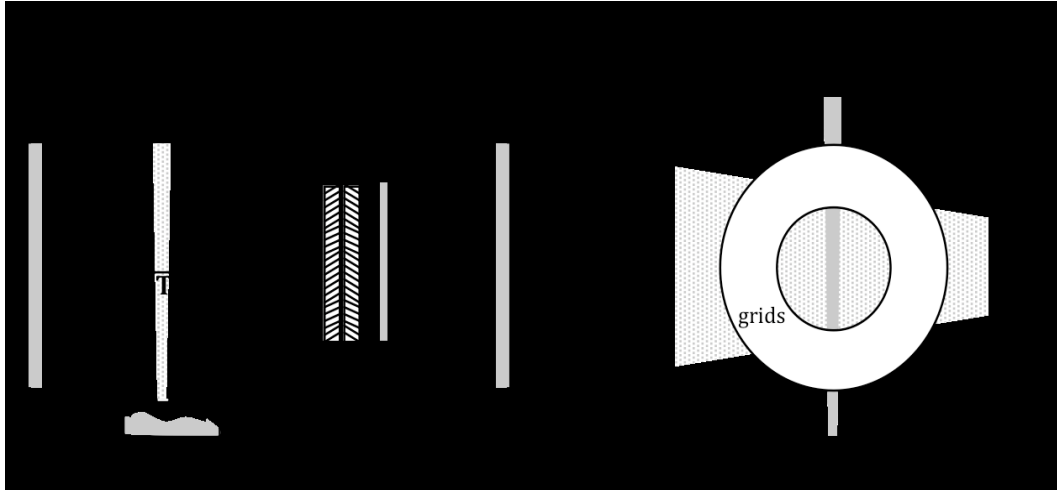


Figure II.E.3. The details of a Rydberg photocathode THz imager.

Our detailed analysis actually showed that the concept was more favorable than we originally proposed and that there are no obvious problems. While such a system would be more complicated than that of the familiar infrared night vision technology, it would appear that it would be considerably less complicated than any of the electronic approaches that have been proposed. This is largely because one does not have to ‘wire’ each pixel individually and that for its readout it would leverage the technology currently being used in the infrared. A summary of these results is provided in Fig. II.E.4.

## Operation Of The System Summary

(Remember: This is for only one choice of operating parameters.)

<b>Target:</b> 10 m away, 1 mW illumination Diffraction limited imaging.
<b>Photocathode active area:</b> 5 cm diameter, 1 mm thick <b>Atomic beam:</b> Cesium, $10^8$ atoms/cc <b>Excitation lasers:</b> 852 nm, 5mW; 518 nm, 30 mW
<b>Frame rate:</b> 30 Hz <b>Frame resolution:</b> 100 pixels x 100 pixels
<b>We find that the photocathode can yield 450 counts/pixel/frame with the noise counts due to the blackbody background under 5. Primary noise contribution is shot noise.</b>

Figure II.E.4. Summary of Rydberg Photocathode approach.



### III. Spin – Offs

#### A. The MACS program.

The work described in section II.A led to the Mission Adaptable Chemical Spectrometer program at DARPA, which was funded via a different ARO contracting vehicle. Here we will briefly describe the results and current status of this project. Briefly put, Phase I of MACS was to develop in 18 months a sensor system in a 1 cu ft volume that could correctly identify with a PFA  $< 10^{-4}$  gases in a mixture made from a library of  $>30$  gases and to be able to demonstrate for one of these gases a detectivity of  $<100$  ppt in an air mixture.

The system shown in Fig. III.A.1 was used to satisfy these goals. The spectrometer (shown in the lower left), frequency control and measurement, data acquisition, system and analysis software, and integration were done by OSU; Battelle provided a very nice compact gas handling and preconcentration system; Enthalpy, Inc. provided gas mixing and handling support; and Smart Transitions, project management, the enclosure, power supplies, and computer cage. While not a partner in the proposal, VDI provided as a vendor the transmitter and receiver used in the system.

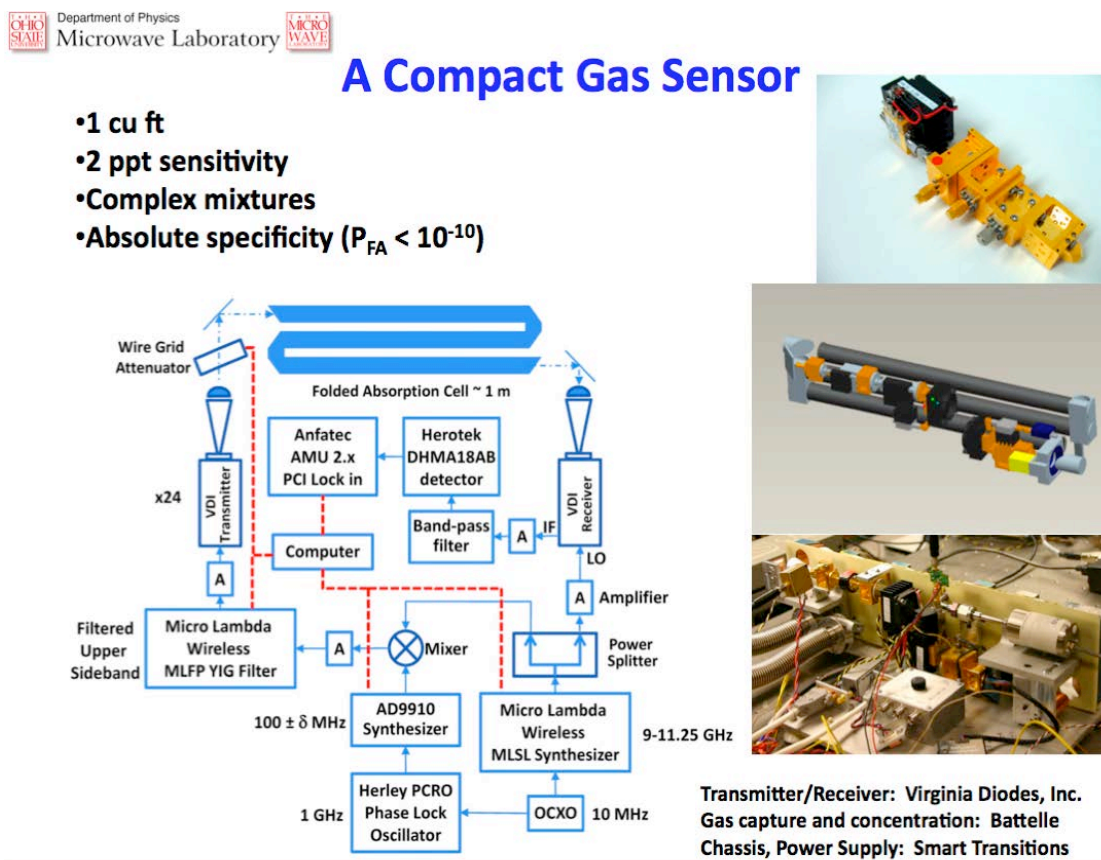


Figure III.A.1. Overview of the MACS Sensor.

This system significantly exceeded the DARPA Go – NoGo requirements of the project. Figure III.A.2. summarizes these results. The sensor strategy that we developed was based on the fact that the SMM fingerprints are ordinarily both highly redundant and sparse. Accordingly, we developed a system with fast frequency agility that could be used to investigate just the spectral space around selected fingerprint lines. While the software would allow for any arbitrary spectroscopic option, we chose to look at small snippets around 6 lines for each species. For the 32 library gases in the example shown in Fig. III.A.2, we looked at a total of 192 such snippets. For convenience of display, we looked at the gases in order of their spectral strength. This system correctly identified (and in addi-

tion quantitatively measured, as shown in the table at the right of the figure) the 14 gases that had been placed (blindly) in this mixture (shown in red), as well as reaction products within the gas mixture (shown in blue). Probability of false alarm is so low that conventional strategies for determining ROC curves do not apply. However, one could show that by any reasonable measure that the probability of false alarm was considerably less than  $10^{-10}$  ( $10^{-4}$  was the Go – NoGo requirement).

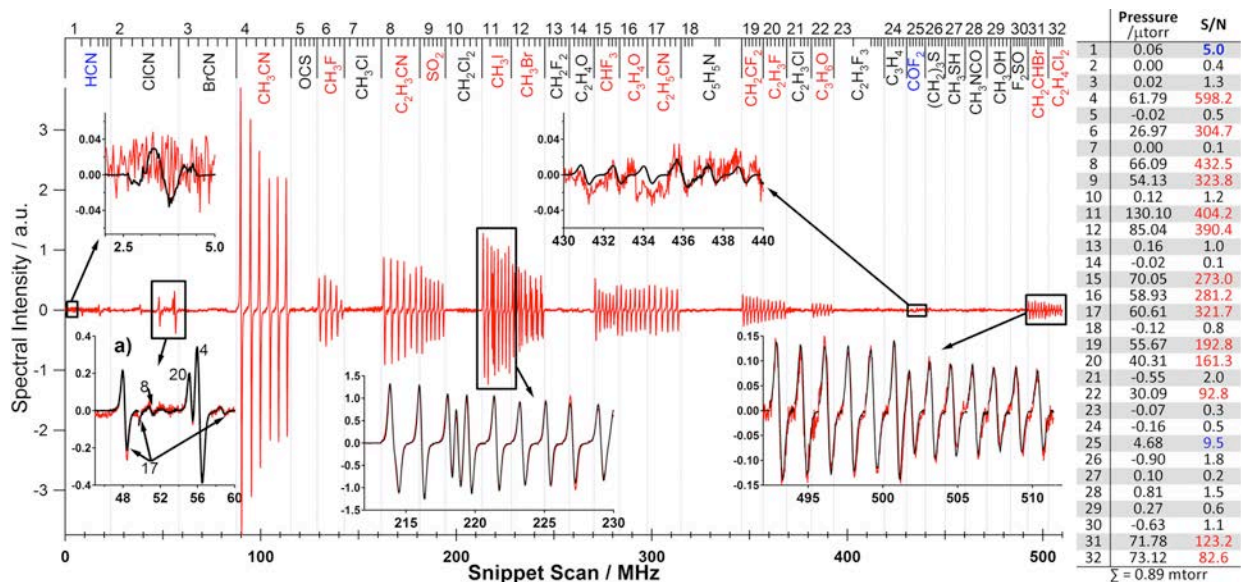


Figure III.A.2. Composite of the gas mixture observation.

Because it was not possible for the agency providing the test samples to accurately provide samples with as small a concentration as we could detect, we agreed on a procedure in which we would detect the minor isotopic concentration of the test species, in this case acetonitrile. Figure III.A.3 shows a spectroscopic observation that corresponds to a detection limit of 2 ppt (the Go – NoGo requirement was 100 ppt).

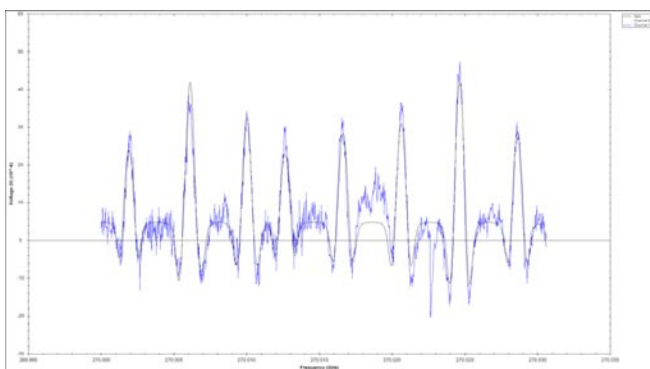


Figure III.A.3 2 ppt detection limit for acetonitrile.

### III.B. SRC CMOS Program (Semiconductor Research Corporation / Texas Instruments)

Perhaps the major impediment to the broad use of the SMM spectral region has been the cost of the basic technology. While this has been largely due to one-of-a-kind systems, the underlying InP and GaAs technologies are still much more expensive than the silicon CMOS that has grown up around the computing industry.

We were approached by a representative of the Semiconductor Research Corporation (who had seen some of our gas sensor work) to see if we were interested in the development of appropriate transmitter, receiver, and related technology in CMOS. Very briefly, we are now involved with three projects at the University of Texas/Dallas to do this. These projects are to develop a transmitter, a receiver, and appropriate antenna structures.

Figure III.B.1 shows an example of a proposed receiver architecture. The scientific driver is that CMOS will have more limitations on power generation as we go to higher SMM frequencies. It appears that this is actually less of a problem for the transmitter (because molecular saturation limits the amount of power that can be used) than it is for the heterodyne local oscillator. The design of Fig. III.B.1 transcends this problem by down converting to an IF frequency that is about half of the signal frequency (thereby reducing the required LO frequency by a factor of 2) and using the capabilities of CMOS to build an IF amplifier at this high frequency.

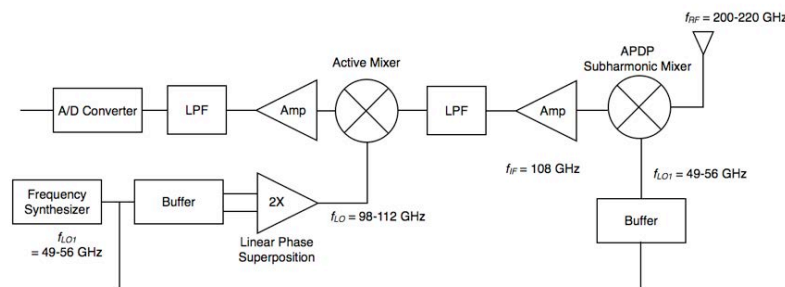


Figure III.D.1. Proposed receiver architecture for CMOS receiver for a gas sensor.

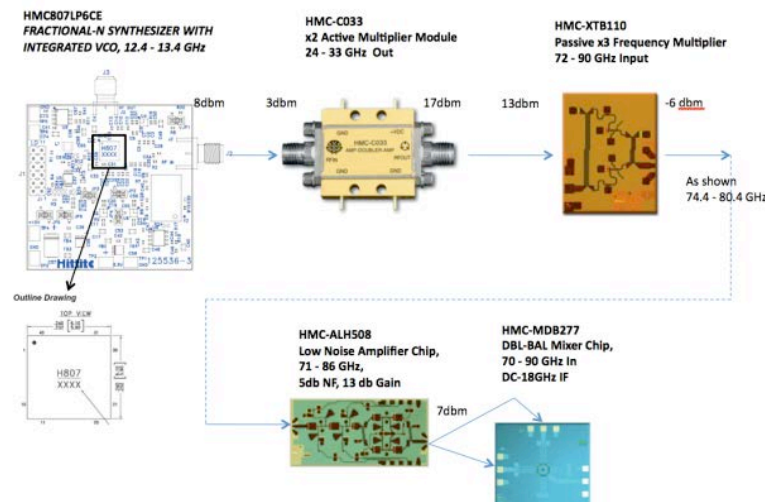


Figure III.D.2. Wireless technology for gas sensor.

Because the development of these circuits will take some time, in parallel we are working to develop demonstration systems using commercial 'wireless' technology. While this does not have the potential for extreme cost savings and integration (the CMOS goal is to even integrate the frequency synthesizer as a part of the chip – for a few dollars!), it is interesting in its own right. Figure III.B.2 shows examples of a chip set and modules currently available from Hittite. We have obtained these chips both in raw form and as modules/evaluation boards (shown in the figure). Since our application requires less power than the wireless communications problem, the critical demonstration for us relates to the spectral purity and sweep/modulation capabilities of the synthesizer. We have now successfully tested these capabilities in the context of a system that multiplies the power to over 600 GHz (a particularly stringent test of spectral purity) with good results.



### **III.C. Terahertz Double Resonance Investigations of High Pressure Gases for Stand-off Chemical Detection (DARPA)**

DARPA has funded a one-year seedling to investigate ideas put forth in Section II.B. The laboratory of Dr. Everitt at ARMDEC is also a part of this project. Key questions for this seedling include:

1. How general is the technique?
  - a. Are there appropriate pump overlaps for species of interest?

We expect that the higher pressure (which gives broader resonances for the pump) and many molecular vibrational fundamentals in the 10  $\mu\text{m}$  region will help a lot.

The preliminary modeling is encouraging and direct measurements are being made.
  - b. Larger Molecules – in the proposal we made spectral density arguments, we plan to (1) do molecular specific spectral simulations, and (2) experimentally confirm these results in the high pump intensity, atmospheric pressure regime.
  - c. The specificity matrix will be the capstone result.

What range of molecules and molecular types will be appropriate?
2. What might impact be of higher order effects?
  - a. Continuum-continuum coupling?
  - b. Coherent effects in the dense spectra of large molecules?
3. Are there practical implementations for scenarios of interest?
  - a. Specificity and Sensitivity in these scenarios.
  - b. Combine the physics above with practical technology.

For such a system to be practical, an appropriate laser needs to be available. In parallel DARPA (with management by Dr. Everitt) has an SBIR underway. STI Optronics has finished its Phase 1 effort. This project has been very successful both in the quality of the modeling and system concepts developed and in the results of this work confirm our more general conclusion that the development of an appropriate laser would be possible. A Phase II SBIR proposal has been funded.

Although we are early in the DARPA Seedling our preliminary results are very favorable. Moreover, we have thought about this for a very long time.

### III.D. Breath Analysis in the THz (DARPA)

Breath analysis is a subject of considerable interest, with entire journals devoted to it. There has been increased interest in the use of spectroscopic techniques and a considerable optical and infrared literature exists. The history of this DARPA Seedling is convoluted, but from DARPA's perspective can be traced to the MACS program. The current effort is rather straightforward, Battelle (the prime on this effort) will select 25 candidate gases that are of biomedical interest and which have potential for sorbent gas capture (which was used by MACS and which Battelle developed). OSU will investigate their suitability for THz detection. The issue will be how rapidly the spectra of the gases of interest become congested or a continuum as their size and complexity is increased. Table III.C.1 shows the results of our experiments to date. In the selection of these molecules we both focused on molecules of interest for breath analysis and those that we thought would be challenging spectroscopically.

Table III.C.1

Compound	Chemical Formula	Relevance as Biomarker for Exposure or Disease	Spectroscopy		Spectrum Resolvable
			Permanent Dipole Moment	Vapor Pressure	
2,5-Dimethyl furan	C <sub>8</sub> H <sub>8</sub> O	Smoking	0.16	155 mm Hg @ 25C	yes
Acetaldehyde	CH <sub>3</sub> C(O)H	Ethanol metabolism, CW precursor or solvent, precursor in illicit drug and explosives manufacture, lung cancer	2.7	800 mm Hg @ 20.3 C	yes
Acetone	CH <sub>3</sub> C(O)CH <sub>3</sub>	Industrial solvent, precursor in explosives or illicit drug manufacture, diabetes	2.91	750 mm Hg @ 20C	yes
Acrolein	CH <sub>2</sub> CHC(O)H	Toxic industrial chemical, air quality concern, precursor in manufacture of explosives	2.5	210 torr @ 20C	yes
Aniline	C <sub>6</sub> H <sub>5</sub> (NH <sub>2</sub> )	Industrial chemical, lung cancer	0.84	0.5kPa @ 20 C	yes
Benzaldehyde	C <sub>6</sub> H <sub>5</sub> CHO	Industrial chemical, air quality concern, CW agent precursor	2.72	1 torr @ 26C	yes
Bromodichloromethane	CH <sub>2</sub> BrCl	Water treatment contaminant, air quality concern	1.31	6.6kPa @ 20C	yes
Chloroethylethyl sulfide (Half-mustard)	CH <sub>3</sub> CH <sub>2</sub> SC <sub>2</sub> H <sub>5</sub>	CW simulant	2.27	44 mm Hg @ 73 C	no (will repeat the measurement)
Dibromochloromethane	CH <sub>2</sub> Br <sub>2</sub> Cl	Water treatment contaminant, air quality concern		76 mm Hg @ 20 C	yes
Dichlorobenzene	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	Common industrial solvent, known breath biomarker	ortho - 2.14 meta - 1.72	1.2 mm Hg @ 20C	1,2 - yes, 1,3 need to record
Dimethyl amine	(CH <sub>3</sub> ) <sub>2</sub> NH	CW synthesis precursor, renal disease	2.78	1292 mm Hg @ 25C	yes
Dimethyl methylphosphonate	C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> P	CW precursor and simulant	2.48	160 Pa @ 25C	no
Dimethyl sulfide (DMS)	CH <sub>3</sub> SC <sub>2</sub> H <sub>5</sub>	Pollutant from petroleum refining, cloud formation, halitosis, periodontal disease	1.5	7.5 psia @ 20C	yes
Dimethyl sulfoxide	CH <sub>3</sub> S(O)CH <sub>3</sub>	Industrial chemical, halitosis	3.96	0.417 mm Hg @ 20 C	yes
Ethaneethiol	CH <sub>3</sub> CH <sub>2</sub> SH	Industrial chemical, air quality concern	1.6	442 @ 20C	yes
Ethanol	C <sub>2</sub> H <sub>5</sub> O	Alcohol consumption, CW synthesis precursor, CW simulant, precursor in illicit drug manufacture	1.69	40 Torr @ 19C	yes
Ethyl acetate	CH <sub>3</sub> C(O)OCH <sub>2</sub> CH <sub>3</sub>	Toxic industrial chemical, precursor in manufacture of explosives	1.78	100 torr @27C	need to record
Formaldehyde	CH <sub>2</sub> (O)	Toxic industrial chemical; atmospheric chemistry; precursor for illicit drugs, explosives, rodenticides; breast, bladder, and prostate cancer indicator	2.332	93.6 mm Hg @ 38 C	yes
Freon 11 (CCl <sub>3</sub> F)	CCl <sub>3</sub> F	Industrial chemical, air quality concern, monitored on ISS	0.45	89kPa @20C	yes
Hydrazine	H <sub>2</sub> NNH <sub>2</sub>	Toxic industrial chemical, air quality concern, precursor in manufacture of explosives, rocket fuel	1.85	14.4 torr @ 25C	need to record
Methyl amine	CH <sub>3</sub> NH <sub>2</sub>	Industrial chemical, renal disease	1.31	27 psi @ 20 C	yes
Methyl salicylate	C <sub>8</sub> H <sub>8</sub> O <sub>2</sub>	Mint flavorant, drug taggant, CW simulant, precursor in illicit drug manufacture	3.32	0.0975 mm Hg @ 20C	no
Monoethanol amine	H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH	Industrial chemical, air quality concern, monitored on ISS	3.04	25 Pa @20C	yes
NO	NO	Asthma biomarker, smog indicator, industrial chemical	0.16	0.04 Pa @ 100K	yes
Thionyl Chloride	S(O)Cl <sub>2</sub>	CW agent precursor	1.45	100 mm Hg @ 21C	yes
Thioxane	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	CW agent degradation product	0.29	5.65 mm Hg @ 25 C	yes
Trichloroethylene	C <sub>2</sub> HCl <sub>3</sub>	Common industrial solvent, known breath biomarker	0.9	155 mm Hg @ 20C	yes
Trifluoroacetic Acid	CF <sub>3</sub> C(O)OH	Toxic industrial chemical, precursor in manufacture of explosives	2.3	107 torr @20C	yes

As this project has evolved, we have been encouraged to broaden our list of molecules to include those of interest for 'chemical intelligence' and we are doing so.

**E. Large Molecules (ARO).** With the end of the MACS program, ARO accepted a proposal to address specifically one of the most important and fundamental scientific issues associated with SMM gas sensors: (1) How large and complicated molecules can this approach be applied to, and (2) what are strategies for maximizing this list of molecules?

The fundamental problem is that the usual SMM/THz spectroscopic strategy depends upon the narrowness of Doppler broadened spectral lines to separate them from broader power variations due to standing waves, etc. Since the latter are typically 10% of the total power and often one seeks to observe spectral lines that have fractional absorptions of  $10^{-7}$  there are six orders of magnitude in sensitivity at stake.

If spectral lines have begun to merge into spectral ‘features’ there are at least two approaches that can gain back some or all of this six orders of magnitude

*Cavity Strategies:* The use of high Q-cavities: Here one regains the sharp spectral feature to measure in the context of a sharp cavity resonance, whose Q and amplitude are both modified by the molecular absorption. In fact, it is possible to observe with great sensitivity weak continuum contributions that are important in long path atmospheric transmission in the THz.<sup>13, 14</sup> Figure III.E.1 shows the cavity spectra of the difluorobenzonitriles. Although

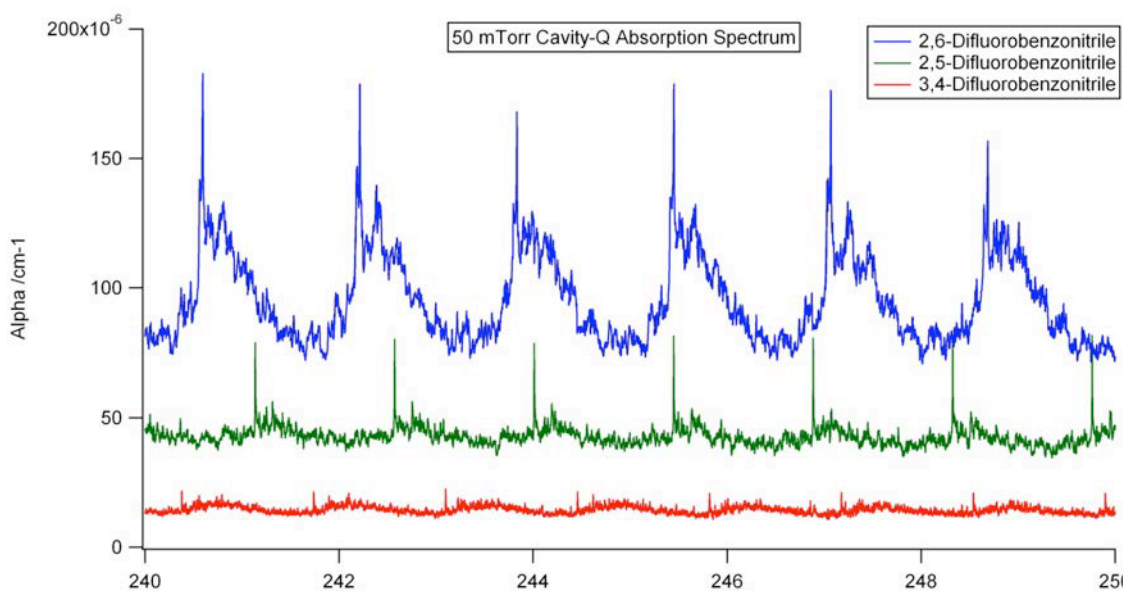


Figure III.E.1. Cavity spectra of the difluorobenzonitriles.

this is a highly compressed scale, it is possible to see individual lines (or at least close clumping of lines) in the red trace of the lightest of these species. However, as one goes to the heaviest, it can be seen that broader features emerge. It should also be noted that these cavity measurements measure *absolute* absorbance and the signal recovery does not depend upon narrow lines. Indeed, it can be seen that all three spectra have considerable continua component, as evidenced by their offset from zero. It should be noted that the heaviest species (shown in blue) should have the weakest lines, where as its ‘features’ are actually the strongest. This results from the overlap of spectral lines, an effect that increases with molecular size. We have discussed this in some detail in an astrophysical context<sup>15</sup> and it can be a path both for astrophysics and terrestrial gas sensors towards the spectroscopic detection of larger species. The most important scientific question is the determination of where this overlap and blending of lines becomes so strong as to reduce the specificity of the remaining ‘features’ for the determination of the chemical composition of the mixture.

*Stark Modulation Strategies:* The sharp spectral features of Doppler limited THz spectroscopy are ordinarily recovered by the imposition on the THz carrier of a small FM modulation whose width is similar to the Doppler width of the line. An alternative is to apply a zero based Stark field that moves the frequency of the spectral line. Because ordinarily the frequency of the Stark shift is inversely proportional to the spectral frequency, this technique is usually used in low frequency (<40 GHz) microwave spectroscopy. However, it can be shown in the THz virtu-

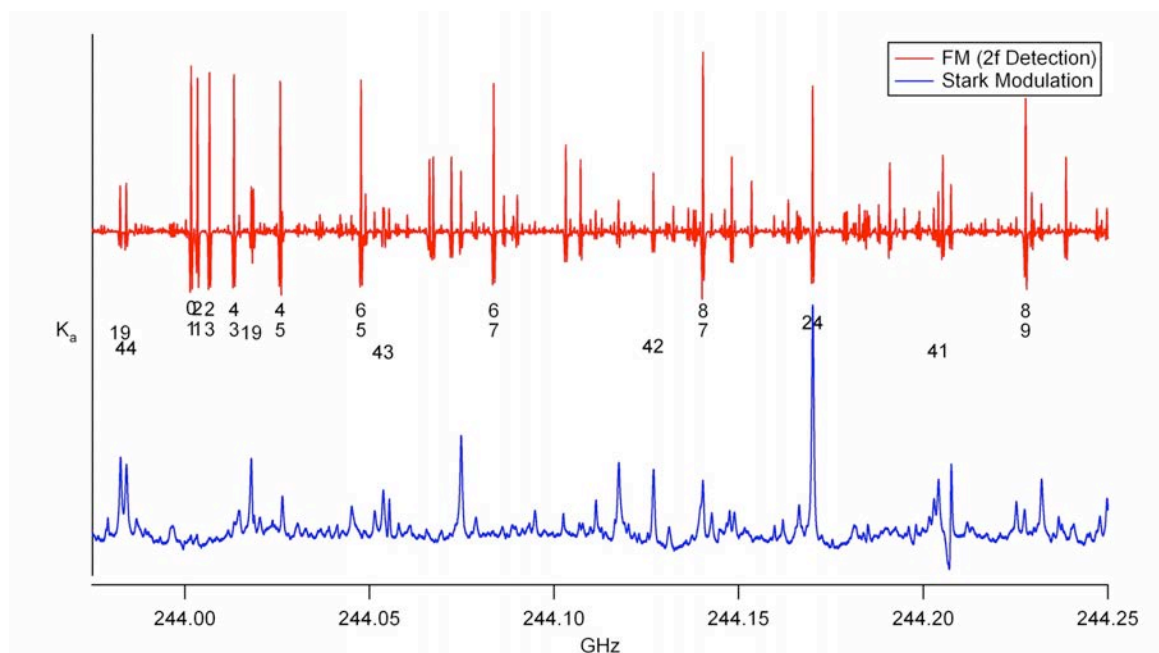


Figure III.E.2. A comparison of and FM modulate spectrum and a Stark modulated spectrum.

ally all large molecules have degeneracies that result in large Stark shifts. While this only applies to a subset of the total spectrum, for a sensor this is actually an advantage in that it results in a less crowded spectrum. Thus, for a sensor we gain two things: (1) the aforementioned reduction in spectral congestion, and (2) a modulation method that does not depend upon narrow Doppler broadened lines. Figure III.E.2 shows an example. An important research frontier for this approach is the determination of when the overlap from the frequency shifted Stark components begins to reduce the efficiency of the Stark modulation.

## IV. Additional Paths

Beyond or in conjunction with the aforementioned spin-off programs there are important paths that can lead to broadly adopted applications of the THz spectral region. Most of these are not conceptually new, but have not been realized because of real gaps in either our physics knowledge of the availability of practical, publically available technology. These include sensors, imaging, and remote sensing. We will consider each in turn.

### A. A Point Sensor Program

If we want to argue that further investment in the sensor direction that emerged from Phase 1 of the MACS program should be considered, at least two considerations should be address: (1) What are its current and potential capabilities relative to alternatives, especially well know ones which have been considered extensively, and (2) What are examples of applications of interest?

Figure IV.A.1 is a copy of a viewgraph that summarizes a comparison with both Op/IR and other SMM/THz



## Where are we Relative to Alternatives?

	Optical Comb/Cavity 100 Torr <sup>1</sup>	SMM 1.5 m Cell 10 mTorr	THz-TDS 5 m White Cell 7.5 mTorr <sup>2</sup>
$\Delta\nu_{\text{system}}$	1600 MHz	0.5 MHz	3000 MHz
$\Delta\nu_{\text{instrument}}$	800 MHz	0.001 MHz	3000 MHz
NH <sub>3</sub>	18 ppb $9.6 \times 10^{-11}$ mole	52 ppb $2.7 \times 10^{-14}$ mole	---
CO	900 ppb $4.8 \times 10^{-9}$ mole	280 ppb $1.5 \times 10^{-11}$ mole	---
HCN	---	10 ppb $5.3 \times 10^{-15}$ mole	---
CH <sub>3</sub> CN	---	50 ppb $2.7 \times 10^{-14}$ mole	---
CH <sub>3</sub> Cl	---	---	$10^9/10^4$ ppb <sup>5</sup> $4 \times 10^{-7}/10^{-12}$ mole

### Optical Comb/Cavity:

- Similar ppx sensitivity
- requires  $10^4$  more sample – sorbent difficult
- has  $>10^4$  lower resolution
- orders of magnitude more atmospheric clutter
- much larger and more complex

### THz-TDS:

- has  $>10^3$  less ppx sensitivity
- requires  $10^6$  more sample – sorbent difficult
- has  $>10^4$  lower resolution
- very sensitive to water interference
- somewhat larger and more complex

### 3G THz Photomixer:

- has  $>10^4$  less ppx sensitivity
- requires  $10^8$  more sample – sorbent difficult
- demonstrates  $>1000$  less resolution
- orders of magnitude more atmospheric clutter
- somewhat larger and more complex (8 cu ft)

•SMM offers 'absolute' specificity

•SMM requires orders of magnitude less sample

=> Sorbents very advantageous, but spectroscopic optimizations unknown

•SMM has unknown limits wrt large molecules

•SMM has clear path to small and inexpensive

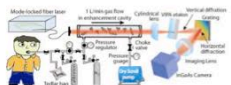
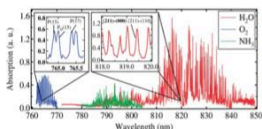


Figure IV.A.1. A comparison overview for point gas sensors.

sensors. Relative to either, the results are favorable by *orders of magnitude*. This is probably not well known because, to the best of our knowledge, while the literature that discusses this other sensor work includes extensive comparisons with itself, it never provides a comparison with cw electronic approaches in the SMM/THz.



**IV.A.1 Optical/Infrared (Op/IR) sensors.** There has been considerable work devoted to the use of laser based optical and infrared spectroscopy as the basis for gas sensors. This work has been reported in the leading journals including Science<sup>16</sup> and Nature.<sup>17</sup> As one of only many examples, Figure IV.A.2 shows a report of this in the popular press.

#### Optical 'Frequency Comb' Can Detect The Breath Of Disease

*ScienceDaily (Feb. 22, 2008)* — Exhale on a cold winter day and you will see the water vapor coming out of your mouth. Light up your breath with a Nobel-Prize-related tool, and you could potentially detect trace amounts of over 1,000 compounds, some of which provide early warning signs of disease. In a new paper,\* a team led by Jun Ye, a physicist at JILA, a joint institute of the National Institute of Standards and Technology (NIST) and the University of Colorado at Boulder, has demonstrated an optical technique for simultaneously identifying tiny amounts of a broad range of molecules in the breath, potentially enabling a fast, low-cost screening tool for disease.

Figure IV.A.2 A press release typical of those describing laser based gas sensors.

THz, and that the clutter limit for the IR optical comb system is typically six orders of magnitude worse. We are preparing a detailed paper on clutter that considered both clean and polluted atmospheres as defined in the literature.<sup>18</sup> It concludes that for cw electronic sensors the clutter limit is well below 1 ppt.

Figures IV.A.1 above shows that in terms of ppx sensitivity the optical comb sensors and the cw electronic SMM/THz sensors are similar (with equal observation time), but that if the figure of merit is the amount of sample required that the SMM/THz cw electronic system is about four orders of magnitude better.

Figure IV.A.3 shows that clutter is an insignificant contributor in the

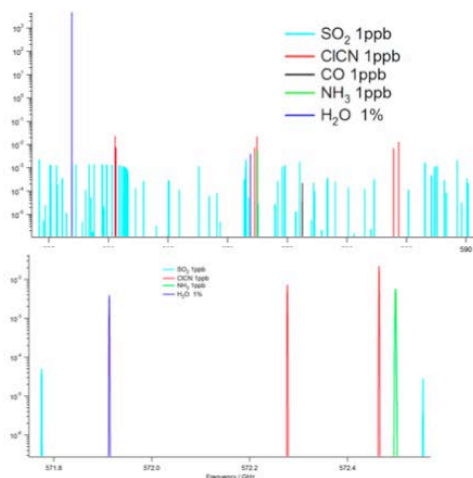


Figure 1. SMM atmospheric spectra of **four species at 1 ppb** in an atmosphere that contains 1% (10<sup>7</sup> ppb) water. The lines are so narrow in the upper graph that the most crowded region is blown up by a factor of ~100 to marginally show the linewidths.

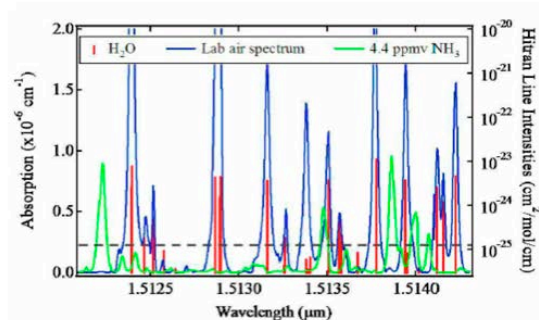


Fig. 7. The absorption spectrum of lab air superimposed over the spectrum of 4.4 ppm of NH<sub>3</sub>. Hitran line intensities for H<sub>2</sub>O are included to identify the absorption features of the lab air spectrum. The dashed grey line represents the typical concentration of NH<sub>3</sub> contained in the breath of a patient at final stages of renal failure.

Figure 2. Fig.7 from the OC paper that shows **NH<sub>3</sub> at 4.4 ppm** in a background of lab air.

Recent work shows that atmospheric clutter limit for most if not all of the MACS 32 molecules is below **1 ppt**

Figure IV.A.3. Clutter comparison between the Op/IR and cw electronic gas sensors.



## IV.A.2 Other THz approaches

There have been many papers published that describe the use of other THz technologies for gas sensors. As we will briefly show below, these approaches (most notably THz-TDS and to a lesser extent photomixers) are inferior by orders of magnitude in both specificity and sensitivity.

The most visible photomixer system is one which has gone through three generations of development and which is shown as an 8 cu ft box in the lower left panel of Fig. IV.A.1.<sup>19, 20</sup> Figure IV.A.2 compares the resolution of this system on one of its chosen species, acrylonitrile. The photomixer spectrum is shown in the right panel (about 8 resolved features per 100 GHz) and a similar width region shown as a series of expansions in a cw electronic system on the left. The cw electronic mixture on the left assumes a concentration of 1 ppb against atmospheric clutter in a



## OSU SMM System vs THz Photomixer System

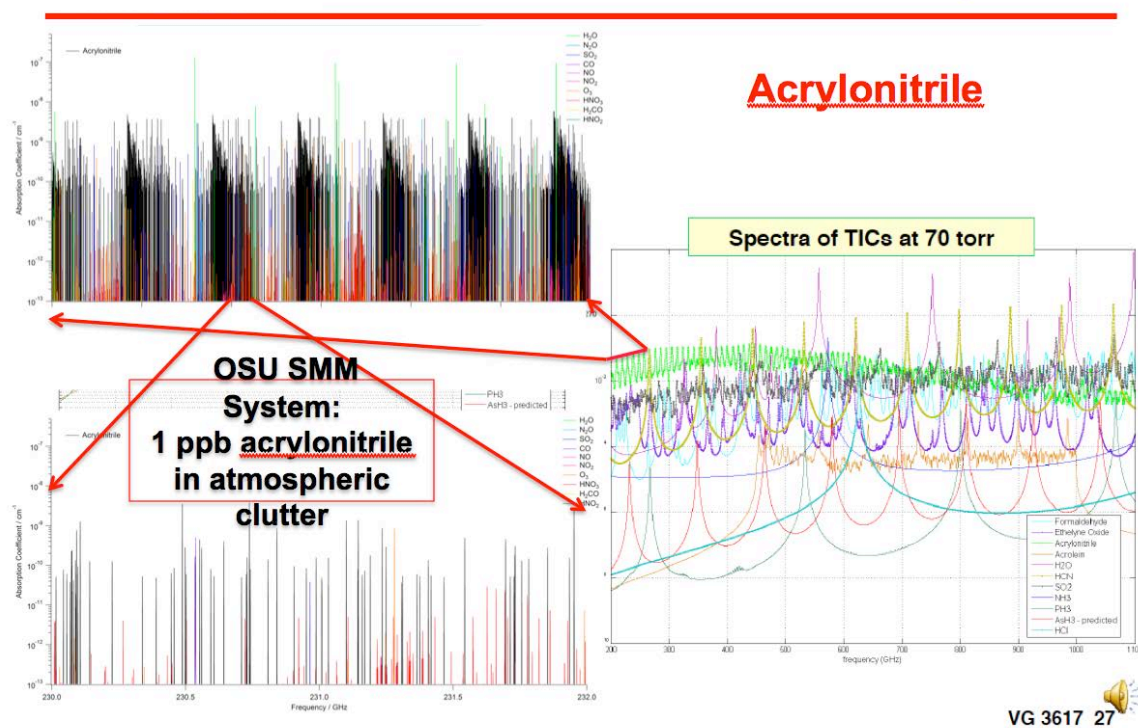


Figure IV.A.4. A double expansion to show the relation between a THz photomixer system and a cw electronic system. The seven spectral clumps of acrylonitrile in the photomixer system are resolved into thousands of individual lines in cw electronic system.

spectral region for which the clutter is worst. Presumably, the difference in the performance of these sensors can be traced to both available power (really spectral brightness) and issues related to calibration and spectral purity. For the PM the 'solution' to this is to work at higher pressure and greater linewidth, which mitigates these problems. Combined with several orders of magnitude less spectroscopic sensitivity, this results in a sensor whose ppx sensitivity is about  $10^4$  less and which has about  $10^8$  less sample sensitivity. They expect further improvements in their system as they undertake the development of a 4<sup>th</sup> generation system.

Since THz-TDS systems are even less favorable, at this point we will simply refer interested readers to the literature.<sup>21, 22</sup>

### IV.A.3 What can Phase 1 MACS do?

While there are many important frontiers associated with research on large molecules (which ARO is currently funding), the current capability of the Phase 1 MACS system is quite impressive. Figure IV.A.3.1 shows a US Army list of Toxic Industrial Chemicals (TICS) and that the large majority of them can be detected with ‘absolute’ specificity.

Chemical	Rate of Onset	Persists in Environment	Thresholds (ppm/hour) Impairment/fatality	BDQ/ Mask Effective	Odor	Related hazards/ Source/ Use	Sensodyne tube (H)	205A series Miran Sapphire	Symptoms (from inhalation and dermal contact)	Decontamination and Treatment
Allyl alcohol (colorless liquid)	Immediate	Days-weeks, +	7.7 / 22	?	Mustard-like	Rapidly absorbed through skin highly flammable with caustic fumes; used as contact pesticide, plastic/perfume manufacture	Not available (liquid)	Not available (liquid)	General Mild Health Effects: - Nausea, dizziness; headaches, chills, coughing, choking, throat irritation	Decontamination: - Flush (15 min) eyes & skin with water; - Soap optional after initial water rinse
Acrolein (colorless-yellow liq)	Immediate	Minutes to hour	0.1 / 1.4	Poor	1 ppm - sharp, acid, sweet	Toxic and corrosive fumes; Herbicide	#93 (BUT high detection)	Not standard	Specific and More Severe Effects: - Irritation; tearing/watering; pain; intolerance to light (e.g. from Hydrogen Sulfide)	Treatment & Diagnostic procedures/ options: - Saline wash - Antibiotic ointments
Acrylonitrile (clear/pale yellow liq)	Immediate	Minutes to HOURS	35 / 75	Poor	17 ppm - unpleasant, sweet (peach)	Flammable gas; used in Plastics, coatings, adhesives industries; dyes, pharmaceuticals	#191	Standard	Eye: - Irritation; tearing/watering; pain; intolerance to light (e.g. from Hydrogen Sulfide)	Eye injuries: - topical corticosteroids and/or antihistamines - Inject MgSO4 at affected site (Hydrogen fluoride)
Ammonia (colorless gas)	Immediate	Minutes to 24 hours	110 / 1100	Poor	17 ppm - sharp, suffocating dry urine	Explosives manufacture; pesticides; detergents industry	#3M	Standard	Skin (particularly if liquid contact): - Irritation; burning; blisters (eg with Hydrogen Fluoride); vesiculation (nitric & sulfuric acid); dermatitis; and frostbite (e.g. Acrylonitrile)	Skin burns/blisters/irritation: - topical corticosteroids and/or antihistamines - Inject MgSO4 at affected site (Hydrogen fluoride)
Arsine (colorless gas)	Immediate	Minutes to hours	0.2 / 0.5	Good	0.5 ppm - garlic-like	Reacts with H2O (don't use H2O in fire). Used in electronics ind	#19L	Not standard	Respiratory Tract/Lungs: - Breathing difficulty; respiratory distress; laryngeal spasm (e.g. from hydrogen chloride or hydrogen bromide); pulmonary edema	Breathing/respiratory distress: - Oxygen & ventilation - Prophylactic antibiotics - Xrays - Pulse ox/blood gas
Chlorine (greenish-yellow gas)	Immediate	Minutes to hours	3 / 22	Good	3.5 ppm - pungent (bleach), suffocating	Irritating corr fumes; heavier than air; Cleaner/disinfectant in many industries; water treatment; WWI war gas.	#80	Not standard	Chest/Heart: - chest pain; tachardia (rapid heartbeat)	NOTE: avoid mouth to mouth to protect against cross contamination
Diborane (colorless gas)	Immediate	Minutes to hours	>1 / 15	Good	2.5 ppm - sickly sweet	Very flammable; Intermediate chemical manufacturing;	#22	Not standard	Systemic; Blood: - Cyanotic (blue skin from lack Oxy to blood) (e.g. from SO2, SO3, NO2, ethylene oxide); Convulsions/seizures - Hemolytic anemia; kidney damage (Arsine)	Bronchospasm/Pulm Edema: - Inhale corticosteroids - Beta2 agonist - Endotracheal intubation
Ethylene oxide (colorless gas/liq)	Immediate	Minutes to hours	45 / 200	Poor	425 ppm - sweet, ether-like	Very flammable; Rocket propellant; fumigant; sterilization in health care industry.	#163L	Standard	Additional Chemical Specific Symptoms: - pink/roth sputum; Ammonia mucoid frothy sputum; SO2,SO3, NO2 peculiar taste: asphyxia; metal taste & or garlic breath Hydrogen Selenide	Hemolysis (e.g. Arsine): - IV, transfusion
Formaldehyde (clear, white gas/liq)	Immediate	Hours	10 / 25	Poor	1 ppm - pungt suffocating	Flammable; Disinfectant/germicide; fungicide; textile; health care (tissue fixing)	#61D (Dosi)	Standard		
Hydrogen bromide (pale yellow liq)	Immediate	Minutes to hours	3 / 30	Good	2 ppm - sharp stinging	Chemical manufacturing industry; very corrosive	#15L	Not standard		
Hydrogen chloride (hydrochloric acid) (pale yellow-colorless liq)	Immediate	Minutes to hours	22 / 104	Good	0.77 ppm - pungent, irritating	Corrosive liquid; One, other metal refining/ cleaning; foodpickling; disinfectant; herbicide; other industries	#80	Not standard		
Hydrogen Cyanide (colorless-white-pale blue gas; liquid <75F)	Immediate	Minutes	7.0 / 15-50	Good	1-5 ppm - bitter/sweet almond-like	Weak acid except in water or mucous membranes - then corrosive/irritating; used as War gas, pesticide, Herbicide; other industries	#12L	Not Standard		
Hydrogen fluoride (colorless gas/fuming liq)	Immediate & Delayed	Minutes to hours	24 / 44	Good	0.4 ppm - strong irritating	Corrosive liq; Aluminum and other metal industries; insecticide manufacturing	#17	Not standard		
Hydrogen selenide (colorless gas)	Immediate	Minutes - Hour	0.2 / 1.5+	Poor	0.3 ppm - decayed horseradish	Highly flammable/explosive; can cause burns/frostbite; decomposes rapidly to form elemental selenium Metals & semiconductor prod.	Not available	Not standard		
Hydrogen sulfide (colorless gas)	Immediate & Delayed	MINUTE S to hours	30 / 100	Good	0.1 ppm - rotten egg	Disinfectant lubricant/oils; intem for HC manufacture; deadens sense of smell	#44	Not standard		See page 2
Methyl hydrazine	Immediate & Delayed (LUNGS)	Hours - days	1.0 / 3.0	Poor?	1-10 ppm - ammonia like	Irritating vapors; Flammable-Once ignited continues to burn; Used as solvent, rocket fuel;	#185	Not standard	General Mild Health Effects: - Nausea, dizziness; headaches, chills, coughing, choking, throat irritation	Decontamination: - Flush (15 min) eyes & skin with water; - Soap optional after initial water rinse
Hydrazine (colorless, oil (fuming) liquid/woxy solid or crystals)	Immediate & Delayed (LUNGS)	Hours - days	13 / 35	Poor?	3-4 ppm - Ammonia -like	Flammable-Once ignited continues to burn; irritating vapors; Used as solvent, rocket fuel;	#3D (Dosi)	Standard	Specific and More Severe Effects: - Irritation; tearing/watering; pain; intolerance to light (e.g. from Hydrogen Sulfide)	Treatment & Diagnostic procedures/ options: - Saline wash - Antibiotic ointments
Methyl isocyanate (colorless liquid)	Immediate	Minutes to hours	0.5 / 5	Poor	2.1 ppm - sharp pungent	Intermediate in manufacturing; reacts with H2O (don't use in fire)	Not available (liquid)	Not standard	Eye: - Irritation; tearing/watering; pain; intolerance to light (e.g. from Hydrogen Sulfide)	Eye injuries: - topical corticosteroids and/or antihistamines - Inject MgSO4 at affected site (Hydrogen fluoride)
Methyl mercaptan (colorless gas; liquid <43F)	Immediate	Minutes to hours	5.0 / 23	Poor	0.002 ppm - rotten cabbage (1 ppm odor fatigue)	From decayed organic matter - pulp mills, oil refineries; highly flammable; liquid burns/frostbite	#71	Not standard	Skin (particularly if liquid contact): - Irritation; burning; blisters (eg with Hydrogen Fluoride); vesiculation (nitric & sulfuric acid); dermatitis; and frostbite (e.g. Acrylonitrile)	Skin burns/blisters/irritation: - topical corticosteroids and/or antihistamines - Inject MgSO4 at affected site (Hydrogen fluoride)
Nitrogen dioxide (colorless gas/pale liq)	Delayed (24-72 hrs)	MINUTES to hours	12 / 20	Poor	1 ppm - ?	Intermediate for manu of nitric acid & sulfuric acid; explosives/rocket propellant	#90 (Dosi)	Not standard	Respiratory Tract/Lungs: - Breathing difficulty; respiratory distress; laryngeal spasm (e.g. from hydrogen chloride or hydrogen bromide); pulmonary edema	Breathing/respiratory distress: - Oxygen & ventilation - Prophylactic antibiotics - Xrays - Pulse ox/blood gas
Nitric Acid (colorless, yellow, or red fuming liquid)	Immediate	Hours-days +	4.0 / 22+	Poor	~1 ppm - Choking, sweet - acid	Used in many industries; Very corrosive to skin/mucous membranes as well as metals & other materials;	#80	Not standard	Systemic; Blood: - Cyanotic (blue skin from lack Oxy to blood) (e.g. from SO2, SO3, NO2, ethylene oxide); Convulsions/seizures - Hemolytic anemia; kidney damage (Arsine) (sulfuric acid, hydrazine)	NOTE: avoid mouth to mouth to protect against cross contamination
Parathion (pale yellow to brown liquid)	Immediate but often Delayed (weeks)	Days to weeks	0.2 / 0.8	Good	0.04 ppm	Organophosphate (insecticide); similar symptoms (and thus treatment) as nerve gases; penetrates leather/canvas and plastics/rubber coatings	Not Available (liquid)	Not Available (liquid)	Chest/Heart: - chest pain; tachardia (rapid heartbeat)	
Phosgene (colorless - light yellow gas)	Immediate & Delayed (LUNGS)	Minutes - HOURS	0.3 / 0.6-5	Good	0.5 ppm - musty hay	Dye, pesticide, and other industries; history as war gas, corrosive/irritating	#16	Standard		
Phosphine (colorless gas)	Immediate & Delayed (LUNGS)	Minutes - hours	0.3 / 1.1-30	Good?	0.9 ppm - rotten fish, garlic	Insecticide; used in manufacture of flame retardants and incendiaries	#7LA	Not Standard		
Sulfuric Acid (clear colorless-brown oily liquid)	Immediate	Hours, days	2.5 / 7.5	Good	Odorless (acid taste)	Toxic fumes when heated Battery/dyes/paper/printing/metals industries, volcanic gas.	Not available (liquid)	Not Available (liquid)	Additional Chemical Specific Symptoms: - pink/roth sputum; Ammonia mucoid frothy sputum; SO2,SO3, NO2 peculiar taste: asphyxia; metal taste & or garlic breath-Hydrogen Selenide Nitosis, sweating, if AChE Parathion coffee-ground vomit - sulfur acid	Hemolysis (e.g. Arsine): - IV, transfusion
Sulfur dioxide; sulfur trioxide, form sulfuric acid (colorless gas)	Immediate & Delayed	MINUTES to hours	>3 / 15-100	Good (SO2); Marginal (SO3)	1 ppm - pungent; metallic taste	Disinfectant and preserving in breweries and food/canning; textile industry; batteries	# 5L	Standard		Seizures: - Diazepam
Toluene diisocyanate (2,4) (water-white to pale yellow liquid, or crystals)	Immediate	Hours - weeks	0.08 / 0.51	Good	0.4-2 ppm - sharp pungent	Skin irritant Polyurethane (wood coatings , foam), nylon industries.	Not Available (liquid)	Not Available (liquid)		

Figure IV.A.3.1. Toxic Industrial Chemical. MACS Phase 1 would have no problem in sorting out and quantifying a mixture that contained *all* of the chemicals marked with the red arrows simultaneously (this would require some library making and inclusion of a band not in the Phase 1 box). Those marked in yellow are probably fine to, but the author does not have personal experience with them. The remaining ‘gases’ have little or no vapor pressure or have no dipole moment.

#### IV.A.4 What is the technical path forward?

Figure IV.A.4.1 summarizes the efforts needed to move forward the general use of the SMM/THz for analytical/sensor purposes. This is labeled 'If I were God' because I understand that this will be done piecemeal, depending upon the interests of sponsors.



Department of Physics

Microwave Laboratory



## If I were God

### I. Clear Evolutionary Paths

#### A. MM/Submm:

VDI, Hittite Module, Hittite Chips, **Integrated CMOS (SRC/TI)**

#### B. Frequency Synthesis:

OEM synthesizer, Hittite evaluation boards, **Hittite chips**

#### C. Computing:

PC cage, laptop, web book, **smart phone equivalent**

#### D. Data input:

NI card in cage/**amfetec** card, USB device/OEM **lockin**, **custom I/O on custom 'smart phone'**

#### E. Vacuum and Pumping

**Diaphram/Turbo**, **small mechanical**, **cell/pump combo**

#### F. Packaging and professionally documented software

### II. Parallel Enhancements and Generalizations

#### A. Sorbent/Spectrometer interplay

Priority even for demonstration and use of current system – not a small task

#### B. Cells:

trades between size and sensitivity

**cells to enhance large molecule performance**

#### C. Alternative system strategies

Double modulation/autodyne; rapid passage; . . .

Red indicates a risk element or unknown

Purple indicates engineering beyond OSU's mission

Figure IV.A.4.1. Paths forward for gas sensors in the SMM/THz. Under each letter heading, the evolutionary path is shown.



#### IV.B. Imaging Phenomenology, Clutter, and Target Signatures

Above we discussed our work in the context of the DARPA TIFT program. At the end of Phase I we had demonstrated a new approach that appeared to be able to produce active images of the quality of passive images, eliminate the problems associated with the requirements for specially ‘posed’ angles, and provide S/N, contrast, and range information ordinarily associated with active imaging/radar. We had also found a number of important features of SMM/Target phenomenology that are unique to the SMM/THz because the scale of the texture of most materials is comparable to the SMM/THz wavelengths. We had also developed what is probably a unique imager at 650 GHz with a 60 cm scanable antenna.

One way to look toward the future is to show the use of our images and work in the context of Mark Rosker’s presentation at IMS2007.<sup>23</sup> Figure IV.B.1 shows a selection of slides from this talk that show the impact of clutter, the need for bandwidth to deal with coherent effects in active illumination, and the need for dynamic range and the means to implement it. One important recent development is that DARPA MTO’s HiFive Program is on track to produce compact, high power (~100 W), broadband TWTs in the 220 GHz window. This will significantly enhance the practicality of the multimode techniques which we have been developing with 1 mW sources. DARPA has provided some additional funding via an ARO vehicle to pursue this work.

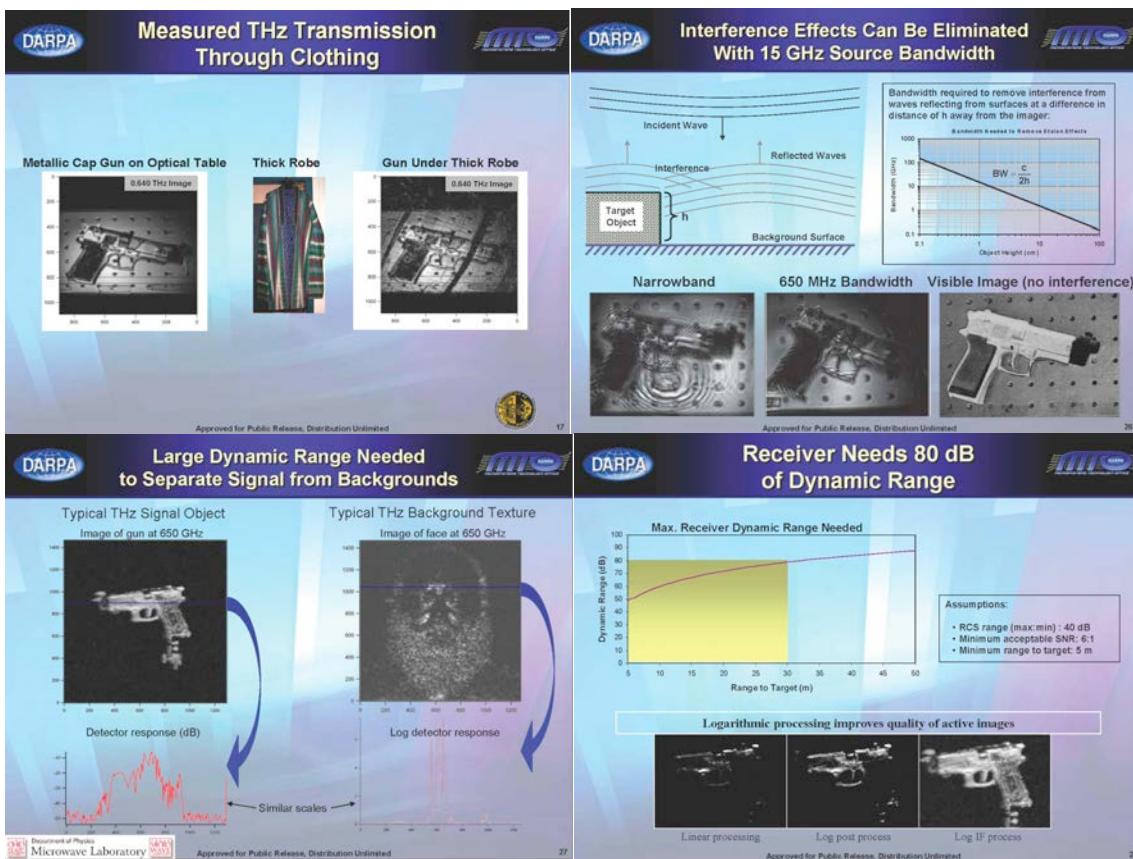


Figure IV.B.1 Selection from imaging workshop slides (courtesy of M. Rosker, DARPA (MTO)).

#### IV.C. The Missile Intercept Problem

SBIR MDA09-034 (Terahertz Signature Modeling for Kill Assessment and Warhead Materials Identification) of the Missile Defense Agency was called to our attention, and we were encouraged to apply. We did so, in collaboration with Applied Quantum Technologies, of Durham, NC, and were awarded a Phase 1 SBIR.

The objective of the SBIR was:

“Develop techniques and tools for high-fidelity, first-principle, chemistry and physics-based modeling of sub mm (Thz) absorption and emission spectra resulting from missile intercept debris fields for threat warhead materials such as nuclear material.”

Since in the context of serving on the External Review Board for Sandia National Laboratory’s THz program, we had been introduced to this problem and had already done calculations and simulations related to this topic, we knew that this was an interesting problem. Very briefly put, kill assessment has here-to-fore been done at very short time by looking at the thermal emission in the optical – primarily atomic. After only a few  $\mu\text{s}$ , the debris field has cooled too much to provide optical or infrared emission. In the summary of our proposal we noted:

“The physical phenomena that dominates the use of submillimeter (SMM) spectra for the analysis of missile intercepts is the rapid cooling of the post-intercept gas and debris field and its impact on the SMM spectral signatures and post-impact chemistry. It is likely that the initial high temperatures and density will result in a molecular soup that is much more complex than the atomic mixtures that provide the short time emission spectra. With this complexity and richness of spectra come the prospects of much more signature specificity, as well as additional information about the physical states of the expanding gas cloud. Although we will vigorously seek government furnished information about the physical and chemical conditions of this late time impact cloud, it appears that much less is known about it than about the early time phenomena that lead to the currently observed atomic flash spectra. *Accordingly, an important aspect of our Phase 1 effort will be to determine if enough information exists or can be developed for the envisioned Phase 2 code development. If not, we will provide alternative paths forward toward that end.* These will emphasize the use of general principles of spectroscopy, chemistry, and remote sensing to establish those points in the evolution of the expanding gas and debris fields that are most likely to provide useful signatures so that resources can be focused on developing the required chemical, spectroscopic, and physical information.”

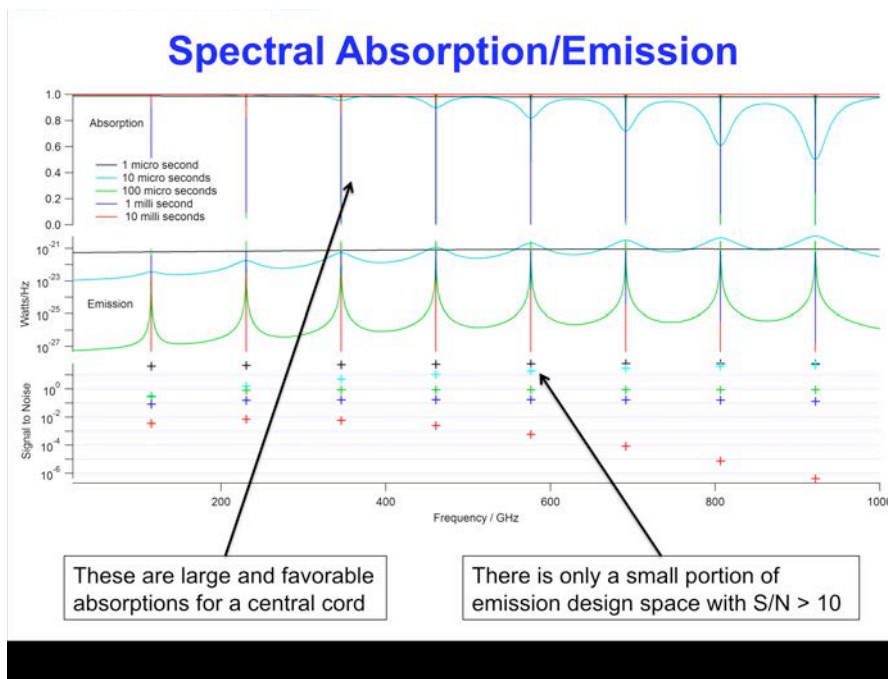


Figure IV.C.1. Thermal emission spectrum as a function of temperature.

We pointed out for Sandia that because of this rapid cooling, this application was not particularly good for the several THz QCLs that they were developing because the cooling caused the signature to be primarily at mm, not THz frequencies. However, this cooling is a two edged sword. While it is true that the absorptions associated with this cold cloud would be in the mm, because the cloud is so cold the emission would be very low. In our preliminary work we have explored this and Figure IV.C.1 shows emission signal as a function of expansion time (lower

panel). The upper panel shows the molecular absorption integrated along a path through the center of the cloud. Fig. IV.C.2 uses the CO result of Fig. IV.C.1 (and adds UO results as well) to show the same result with active illumination.

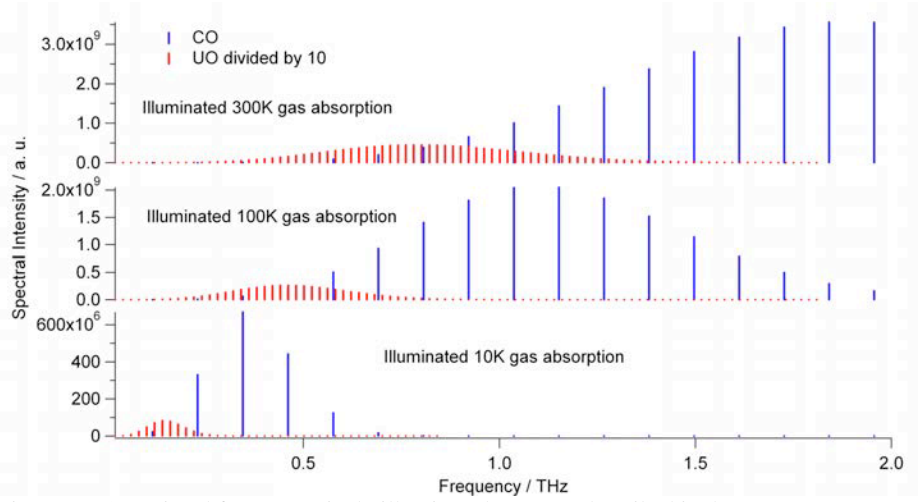


Figure IV.C.2. Signal from an actively illuminated target as described in the text. For comparison the maximum in the emission shown in Fig. IV.C.1 corresponds to about 100 in the scale of this figure.

Inspection of the strength axis shows that at 10 K, the active case is about  $10^8$  more favorable. We were led to consider this active illumination by a very simple calculation that showed that even if the spectral signals were optically thick, that the emission from the 10 K cloud would be marginally detectable on the time scale associated the expansion of the debris field. This expectation was confirmed by the more detailed model of Fig. IV.C.1.

While the goal of Phase I SBIRs is to obtain a Phase 2 SBIR, you will note in our summary above we say that it is highly unlikely that there is enough known about the chemistry, physics, and spectroscopy of this very interesting problem to proceed to the envisioned code writing in Phase 2. If so, and if the THz still looks viable as a solution to this problem, we will suggest developing the required knowledge, but it is unclear if a Phase 2 SBIR is an appropriate mechanism.



## V. Summary

This work, which has extended over about a decade and been sponsored by several agencies, is united by its foundation in SMM/THz science and technology. Much of its motivation has been the desire to exploit this spectral region for sensor applications. This work has included point sensors, non-spectroscopic imaging, remote sensing, and new exo-atmospheric applications, in descending order of maturity. For each we will briefly summarize where we are.

### A. Chemical Point Sensors

For current technology the design space that relates specificity, sensitivity, size, and cost has been established, to include systems with unique and important capabilities. Important research frontiers include establishing the large molecule limits of this technique and developing methods to expand these frontiers. There are clear development paths to a multitude of systems with unique and important capabilities that are compact and very inexpensive. It is clear to us that a SMM/THz point sensor technology will emerge, the main question is the time scale. This area relates to central theme of our laboratory for many decades and a specific focus for at least ten years. We believe in it and will seek to push this application forward.

### B. Non-spectroscopic Imaging

If one is expansive about the lower frequency limit of the SMM/THz, this application has arrived with the advent of airport scanners. This issue of interest to us is how rapidly these applications will evolve to higher frequencies. We simply note here that penetration is a much steeper function of frequency than is often appreciated, and that the phenomenology associated with target signature in the region around 1 THz is very different than at mm or cm wavelengths because of issues involving surface texture. We have made what we think are some original and important contributions to this.

### C. Atmospheric Remote Sensing

With ARO encouragement to ‘think hard’ about the fundamental problems of atmospheric remote sensing (many of which are related to atmospheric pressure broadening), we proposed a double resonance idea more than a decade ago. At that time we did not push for a significant research program because it seemed like the idea was ahead of the technology. Technology developments of the past several years have made a more active pursuit of this approach feasible. We have in place a DARPA seedling to investigate the underlying physics experimentally. Some additional funding could significantly reduce the error bars on a ‘high risk – high payoff’ proposal.

### D. The Exo-atmospheric Intercept Problem.

The physics of the rapidly expanding and cooling debris field that results for an exo-atmospheric intercept is well tuned to SMM/THz remote sensing *qualitatively*. Our work on this and previous ARO programs (Millimeter and submillimeter spectroscopy of non-ambient environments) well positioned us to first advise Sandia on this subject while serving on the External Advisory Board of their THz program and to respond (along with Drs. Guenther and Lontz of Applied Quantum Technologies) to a recent Missile Defense Agency SBIR request. The Phase 1 effort that will result should make it possible to explore this issue *quantitatively*.

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